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CORRECTION

Canadian Journal of Chemistry. Vol. 34, p. 257. In paragraph 2 (below Table II), the first sentence should read: "A weighted average gives a value of $(3.73 \pm 0.05) \times 10^5$ yr. for the α half-life of Pu^{242}."

Canadian Journal of Chemistry

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VOLUME 34 MAY 1956 NUMBER 5

A NEW METHOD FOR PREPARING HYDROXYETHYL ETHERS OF GLUCOSE[1]

BY W. P. SHYLUK[2] AND T. E. TIMELL

ABSTRACT

Three monosubstituted hydroxyethyl ethers of D-glucose have been synthesized by a novel method involving reduction of the corresponding carboxymethyl derivatives with lithium aluminum hydride. This technique also allowed introduction for the first time of hydroxyethyl substituents containing polyethylene oxide chains of a definite length in the glucose molecule, as exemplified by the synthesis of 3-*O*-hydroxyethoxyethyl-D-glucose.

The quantitative paper chromatographic technique has recently been applied to distribution studies on hydroxyethylcellulose (1). In order to obtain the hydroxyethyl derivatives of glucose which were needed as reference compounds, a glucose derivative with the appropriate hydroxyl groups unsubstituted was reacted with ethylene oxide in the presence of alkali. This method of preparation was, however, hampered by the fact that further reaction of the hydroxyethyl group to give polyethylene oxide substituents could not be controlled.

$$ROCH_2CH_2OH + n\overset{O}{\diagup\diagdown}CH_2{-}CH_2 \rightarrow RO(CH_2CH_2O)_nCH_2CH_2OH$$

The synthesis of some carboxymethyl derivatives of glucose has recently been described (3). It has been found that the intermediates which were used for this purpose can be converted by reduction with lithium aluminum hydride into the corresponding hydroxyethyl derivatives of glucose. By repeated carboxymethylation and reduction of the latter, polyethylene oxide substituents of definite length can also be introduced.

$$ROCH_2\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow{LiAlH_4} ROCH_2CH_2OH \xrightarrow[2.\ BrCH_2\overset{O}{\overset{\|}{C}}OCH_3]{1.\quad Na} ROCH_2CH_2OCH_2\overset{O}{\overset{\|}{C}}OCH_3$$

$$\xrightarrow{LiAlH_4} ROCH_2CH_2OCH_2CH_2OH \quad \text{etc.}$$

Thus, reduction of 3-*O*-carboxymethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose methyl ester (3) with lithium aluminum hydride in ethyl ether gave the corresponding hydroxyethyl derivative as a sirup. The latter was hydro-

[1]*Manuscript received December 27, 1955.*
Contribution from McGill University and Pulp and Paper Research Institute of Canada, Montreal, Quebec.

[2]*Present address: Hercules Powder Company, Wilmington, Del., U.S.A.*

lyzed to give 3-*O*-hydroxyethyl-D-glucose which gave only one spot on a paper chromatogram, corresponding to that for Creamer's (2) 3-*O*-hydroxyethyl-D-glucose. The seeds required for crystallizing the sirupy product were obtained by purification on a paper chromatogram.

Reaction of 3-*O*-hydroxyethyl-1,2;5,6-di-*O*-isopropylidene-D-glucose with sodium and methyl bromoacetate in the manner described before (3), followed by reduction, yielded 3-*O*-hydroxyethoxyethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose as a sirup. This compound was hydrolyzed to give a sirupy 3-*O*-hydroxyethoxyethyl-D-glucose which moved slightly faster on a paper chromatogram than a trace of unreacted 3-*O*-hydroxyethyl-D-glucose, no complete separation being effected, however.

A sirupy sample of methyl 3,5,6-tri-*O*-benzyl-2-*O*-carboxymethyl-α,β-D-glucofuranoside methyl ester (3) was reduced in the same manner. The corresponding hydroxyethyl derivative thus obtained was hydrogenated for removal of the benzyl groups and subsequently hydrolyzed to give 2-*O*-hydroxyethyl-D-glucose as a sirup, which, after fermentation, showed only one spot on a paper chromatogram.

Reduction of 6-*O*-carboxymethyl-1,2;3,5-di-*O*-methylene-D-glucofuranose methyl ester and subsequent hydrolysis yielded 6-*O*-hydroxyethyl-D-glucose as a sirup which gave only one spot on a paper chromatogram. This material was crystallized by means of seeds which were obtained after purification by paper chromatography. Brownell (1) had prepared this derivative by a different method, but was unable to crystallize the product.

As is shown in Fig. 1, the three *O*-hydroxyethyl-D-glucoses could be completely separated by paper chromatography, the best solvent system being a mixture of ethyl acetate, acetic acid, and water in the (v/v) ratio of 9:2:2.

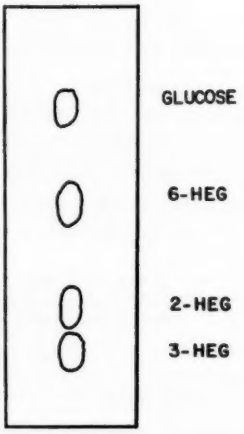

FIG. 1. Paper chromatogram of D-glucose and three *O*-hydroxyethyl-D-glucoses (HEG).

EXPERIMENTAL

Chromatograms were run by the descending method using (1) *n*-butanol saturated with water; (2) ethyl acetate, pyridine, and water, 5:2:5; and (3) ethyl acetate, acetic acid, and water, 9:2:2. Aniline phosphate was used as the spraying reagent. Melting points were determined as referred to earlier (3).

3-O-Hydroxyethyl-D-glucose

To a solution of 3 gm. of 3-*O*-carboxymethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose methyl ester (3) in 50 ml. of absolute ethyl ether, an ether solution of lithium aluminum hydride was added dropwise with stirring in an atmosphere of nitrogen. After three hours at room temperature, anhydrous ethyl acetate was slowly added to decompose the excess of the hydride. Wet ethyl ether was slowly added until a coarse crystalline mass separated, after which approximately 0.5 ml. of water was added. The mixture was dried with sodium sulphate and filtered. Evaporation of the ether solution gave 2.1 gm. of a sirup, which was hydrolyzed with 2% sulphuric acid and deionized with Amberlite IR-120 and IR-4B exchange resins. Evaporation of the neutral solution *in vacuo* yielded a sirup which was found by paper chromatography (solvents No. 1 and 2) to give as the only spot one which corresponded to Creamer's sample of 3-*O*-hydroxyethyl-D-glucose.

Approximately 70 mgm. of the above sirup was applied to a sheet of 3MM paper in spots of 0.005 ml. each, after which the sheet was irrigated with solvent No. 1 for two days. Guide strips were cut from the ends, sprayed, and then used for locating the band on the remainder of the sheet, which was cut out and eluted with water. The aqueous solution was concentrated *in vacuo* to a white residue which was extracted with 2 ml. of absolute ethanol. The latter solution was evaporated to dryness, giving a sirup which crystallized when rubbed with ethanol. Further crystallization with the aid of these crystals as seeds gave 0.78 gm. of crystalline material, m.p. 122–124° C., corresponding to a yield of 50% based on the weight of the sirup hydrolyzed. Recrystallization from ethanol gave 0.40 gm. of a product, m.p. 125–126° C., $[\alpha]_D$ after 3 min., 82.8°, and at equilibrium, 51.8° (*c*, 1.4 in water). Brownell (1) reported an extrapolated initial value of 93° and an equilibrium value of 51.4° for $[\alpha]_D$.

3-O-Hydroxyethoxyethyl-D-glucose

A dry sirup of 3-*O*-hydroxyethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose, 1.4 gm., prepared as described above, was dissolved in 50 ml. of absolute ethyl ether and stirred with 2 ml. of dispersed sodium for 15 hr. at room temperature in an atmosphere of nitrogen. Methyl bromoacetate, 4 ml., was added, the color turning green with evolution of heat, after which the mixture was stirred for six hours at room temperature. Water, 50 ml., and ethyl ether, 50 ml., were added. The ether layer was washed twice with 25-ml. portions of water, dried over sodium sulphate, and evaporated *in vacuo* to a sirup weighing 2 gm., which was subsequently reduced with lithium aluminum hydride in absolute ethyl ether as described above. The sirupy product was hydrolyzed with 4 gm. of Amberlite IR-120 exchange resin and 8 ml. of water at reflux temperature for 12 hr. The aqueous filtrate obtained after removal of the resin

was concentrated to 1.5 ml. Paper chromatography (solvent No. 3) indicated a strong spot which was not completely separated from a weaker, slower moving spot, corresponding to that of 3-*O*-hydroxyethyl-D-glucose. When the latter compound was applied together with the reaction product, the slower moving spot became stronger while the intensity of the faster moving one appeared unchanged.

2-O-Hydroxyethyl-D-glucose

Crude, sirupy methyl 3,5,6-tri-*O*-benzyl-2-*O*-carboxymethyl-α,β-D-glucofuranoside methyl ester (3), 1.0 gm., was dissolved in 10 ml. of absolute tetrahydrofuran and an excess of lithium aluminum hydride was added. After the mixture had been refluxed for 3.5 hr., 0.8 gm. of material was isolated as described for the 3-*O*-hydroxyethyl derivative. The sirup obtained was hydrogenated at a pressure of slightly more than 1 atm. of hydrogen in 20 ml. of tetrahydrofuran in the presence of 0.3 gm. of palladium black at room temperature. The catalyst was removed by filtration and the filtrate was concentrated *in vacuo* to a sirup which was hydrolyzed in the usual way with Amberlite IR-120 exchange resin. Paper chromatography (solvent No. 3) indicated a strong spot which was assigned to 2-*O*-hydroxyethyl-D-glucose and a medium spot for glucose, which disappeared after fermentation of the aqueous solution. No attempt was made to purify this glucose derivative.

6-O-Hydroxyethyl-D-glucose

An excess of ethyl ether solution of lithium aluminum hydride was added to a solution of 1.8 gm. of 6-*O*-carboxymethyl-1,2;3,5-di-*O*-methylene-D-glucofuranose methyl ester in 50 ml. of absolute tetrahydrofuran and the mixture was refluxed for two hours under dry nitrogen. The reaction product was isolated as described for 3-*O*-hydroxyethyl-D-glucose. The sirup obtained, 1.2 gm., was refluxed with 20 ml. of 2.5% hydrochloric acid for 12 hr. The yellow solution was deionized with Amberlite IR-120 and IR-4B exchange resins, treated with Darco G-60, and evaporated *in vacuo* at 45° C. to a sirup. Crystals were obtained by applying 90 mgm. of the latter to a sheet of Whatman No. 3MM paper and by following the chromatographic procedure described above. The remaining sirup was dissolved in 0.5 ml. of ethanol, seeded, and allowed to crystallize at room temperature, resulting in 0.47 gm. of material in 32% yield, m.p. 94–101° C. Recrystallization from ethanol gave 0.16 gm. of a product, m.p. 106–107° C., $[\alpha]_D$ after 4 min., 83.5°, at equilibrium, 48.7° (*c*, 1.5 in water). Calc. for $C_8H_{16}O_7$: C, 42.8; H, 7.14%. Found: C, 42.8; H, 7.09%.

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SYNTHESIS OF FOUR CARBOXYMETHYL ETHERS OF GLUCOSE[1]

By W. P. Shyluk[2] and T. E. Timell

ABSTRACT

The 2-, 3-, and 6-*O*-carboxymethyl-D-glucoses and the 2,3-di-*O*-carboxymethyl-D-glucose have been synthesized. A solvent system was found which gave complete paper chromatographic separation of these derivatives as well as of those obtained upon hydrolysis of a carboxymethylcellulose.

The physical and chemical properties of partially substituted cellulose derivatives cannot be explained only in terms of molecular weight, polymolecularity, and degree of substitution, the distribution of the substituents along the chain molecules of cellulose also having to be considered. Various approaches in such distribution studies have been used, the most direct of which involves quantitative paper chromatography. Brownell (3) appears to have come the closest to a successful application of such a method in his work on hydroxyethylcellulose. However, in this study, as well as in similar work on methylcellulose (1, 8, 11), most of the isomeric mono- and di-substituted derivatives of glucose could not be separated.

Previous investigations on carboxymethylcellulose (6, 12, 15, 16) have indicated the desirability of a more direct approach and this study was undertaken to develop the quantitative paper chromatographic technique for this purpose. Three stages had to be considered in this connection, namely hydrolysis of the carboxymethylcellulose, separation and identification of the various carboxymethylated glucoses in the hydrolyzate, and the quantitative determination of these glucose derivatives.

The hydrolysis of carboxymethylcellulose and the stability of the carboxymethyl group to the conditions of acid hydrolysis have been previously investigated (15). For separation and identification of the seven possible carboxymethyl derivatives of glucose which conceivably could be formed by hydrolysis of a partially substituted carboxymethylcellulose, it was necessary to have these seven compounds available. The present study deals with the synthesis and separation of the 2-, 3-, and 6-*O*-carboxymethyl-D-glucoses and the 2,3-di-*O*-carboxymethyl-D-glucose.

RESULTS AND DISCUSSION

The general procedure used for introducing the carboxymethyl groups in the desired positions was to allow methyl bromoacetate to react with the sodio compound, prepared by the reaction of metallic sodium with a glucose derivative having the appropriate hydroxyl groups unsubstituted. For the preparation of the sodio derivative, advantage was taken of the greater chemical reactivity of sodium dispersions (2). Such dispersions consist of a stable sus-

[1]*Manuscript received December 27, 1955.*
Contribution from McGill University and Pulp and Paper Research Institute of Canada, Montreal, Quebec.
[2]*Present address: Hercules Powder Company, Wilmington, Del., U.S.A.*

pension of microscopic particles of sodium in an inert medium which has almost the same fluidity as the latter, the handling of metallic sodium thus being greatly simplified as a burette or pipette can be used. A microcrystalline semi-dispersion of sodium hydride in oil was also used for the same purpose. This reagent was very similar in its handling and chemical reactivity to the sodium dispersions, having the added advantage of being available commercially.

The following sequence of reactions was used to prepare 3-*O*-carboxymethyl-D-glucose. Reaction of 1,2;5,6-di-*O*-isopropylidene-D-glucofuranose with dispersed sodium in ethyl ether gave the corresponding sodio derivative. The latter was not isolated and an excess of methyl bromoacetate was added to the reaction mixture. Crystalline 3-*O*-carboxymethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose methyl ester was isolated in 61% yield. The same crystalline derivative was also obtained in a somewhat improved yield by the use of sodium hydride in oil. Hydrolysis gave 3-*O*-carboxymethyl-D-glucose as a sirup which was pure as indicated by paper chromatography.

Various analyses of the sirupy 3-*O*-carboxymethyl-D-glucose indicated that it was reasonably pure and the product obtained by treatment of this derivative with methanolic hydrogen chloride also had the correct analysis. The sample could not be induced to crystallize, however, although various techniques were tried. It seemed probable that the main factor preventing its crystallization was to be found in the complex equilibrium mixture existing in its aqueous solution, involving the α- and β-modifications of the furanose and pyranose forms in equilibrium with the *aldehydo* form as well as the two δ-lactones in the 2- and 4-positions.

For the synthesis of 2-*O*-carboxymethyl-D-glucose, a series of reactions similar to that applied by Weygand and Trauth (18) for the preparation of 2-*O*-methyl-D-glucose was used. Treatment of methyl 3,5,6-tri-*O*-benzyl-α,β-D-glucofuranoside with dispersed sodium in ethyl ether resulted in the sodio derivative, which was treated with methyl bromoacetate to give sirupy methyl 3,5,6-tri-*O*-benzyl-2-*O*-carboxymethyl-α,β-D-glucofuranoside methyl ester. Sirupy 2-*O*-carboxymethyl-D-glucose was obtained after hydrogenolysis of the latter compound, followed by acid hydrolysis and purification by adsorption on Amberlite IR-4B exchange resin and thorough washing with water. The regenerated sugar acid contained only a trace of glucose but failed to crystallize. Crystalline methyl 4,6-*O*-ethylidene-β-D-glucopyranoside 3-nitrate was also prepared in the hope that it might be used for obtaining the corresponding 2-*O*-carboxymethyl methyl ester derivative in the crystalline form. The nitrate group, however, was found to be unstable to metallic sodium.

Dimethylene glucose, the structure of which has recently been shown to be 1,2;3,5-di-*O*-methylene-D-glucofuranose (13, 14), has been used for the introduction of substituents in the 6-position of glucose (3, 9). Treatment of this derivative with dispersed sodium in dioxane gave the corresponding sodio derivative which, upon reaction with methyl bromoacetate, yielded 6-*O*-carboxymethyl-1,2;3,5-di-*O*-methylene-D-glucofuranose methyl ester in the crystalline form. Hydrolysis of the latter compound produced a chromatographically pure 6-*O*-carboxymethyl-D-glucose, which could not, however, be induced to crystallize.

In an attempt to establish whether the Purdie reaction could be applied in the synthesis of carboxymethyl derivatives of glucose, dimethylene glucose was treated twice with methyl bromoacetate and silver oxide. A paper chromatogram showed two spots of equal intensity for 6-*O*-carboxymethyl-D-glucose and glucose after hydrolysis, thus indicating the feasibility of the procedure.

For preparation of 2,3-di-*O*-carboxymethyl-D-glucose the following reactions were used. Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside was treated with dispersed sodium to give the disodio derivative which was subsequently allowed to react with methyl bromoacetate to yield methyl 4,6-*O*-benzylidene-2,3-di-*O*-carboxymethyl-α-D-glucopyranoside methyl ester as a sirup. A paper chromatogram of the hydrolyzed material exhibited weak spots for 2-*O*-carboxymethyl-D-glucose and glucose, and an additional strong spot which was assumed to represent 2,3-di-*O*-carboxymethyl-D-glucose. Better results were obtained with sodium hydride but the Purdie reaction gave only a trace of disubstituted compound.

As shown in Fig. 1, a complete separation of the *O*-carboxymethyl-D-glucoses by paper chromatography was accomplished. As far as is known, this appears

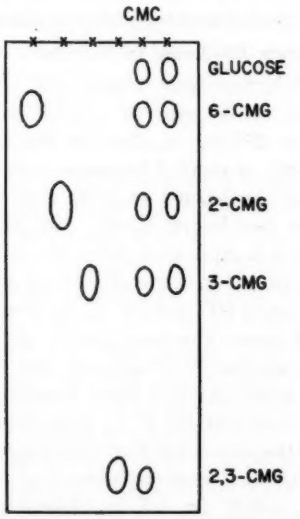

FIG. 1. Paper chromatogram of D-glucose, four *O*-carboxymethly-D-glucoses (CMG), and hydrolyzate of a carboxymethylcellulose (CMC).

to be the first instance when three isomeric monosubstituted glucose derivatives have been unambiguously separated on a paper chromatogram. The solvent system which gave this separation was composed of ethyl acetate, formic acid (87–90%), and water in the (v/v) ratio of 12: 1: 12.

The carboxymethylcellulose referred to in Fig. 1 was a specimen averaging 1.11 carboxymethyl groups per anhydroglucose unit of the chain molecules. This compound, when hydrolyzed and subjected to paper chromatography,

gave the spots indicated, the intensity of which suggested the correctness of a previous, indirect analysis of the same sample (16). With only one disubstituted carboxymethyl glucose available nothing, of course, could be stated yet concerning the presence and nature of the disubstituted sugars present in the hydrolyzate.

EXPERIMENTAL

Although two samples of dispersed sodium were kindly supplied by U.S. Industrial Chemical Company, New York, N.Y., most of the dispersed sodium was prepared shortly before use with the aid of a Waring Blendor with a modified Pyrex jar (2). A 20% microcrystalline semidispersion of sodium hydride in Bayol 85 was obtained as a sample through the courtesy of Metal Hydrides Inc., Beverly, Mass.

For paper chromatography, the descending flow technique was applied throughout and the solvent system was the mixture mentioned above. The chromatograms were made on Whatman No. 3MM paper and aniline phosphate (4) was used to locate the spots. The thermometer employed for determining the melting points was checked against pure compounds as suggested by Bunce (5) and all values were corrected accordingly.

3-O-Carboxymethyl-1,2;5,6-di-O-isopropylidene-D-glucofuranose Methyl Ester

A. Method Using Sodium Dispersed in Toluene

An excess of dispersed sodium was added with constant stirring and in an atmosphere of nitrogen to 60 gm. of 1,2;5,6-di-*O*-isopropylidene-D-glucofuranose (17) dissolved in 575 ml. of absolute ethyl ether. After six hours at room temperature, 35.6 ml. of methyl bromoacetate was added dropwise from a burette and a vigorous exothermic reaction was observed, after which the mixture was refluxed for two hours. Water, 100 ml., was added and the resulting red aqueous layer was separated. After the ether layer had been washed with four 50-ml. portions of water, it was dried over anhydrous sodium sulphate and concentrated *in vacuo* at 50° and 75° C. to give 73.0 gm. of a crystalline product. Hydrolysis and paper chromatography showed a strong spot which was assigned to 3-*O*-carboxymethyl-D-glucose and a weak spot for glucose. Recrystallization of the crude product from isopropyl ether gave 46.7 gm. of material in 61% yield, m.p. 100–101.5° C. Four more recrystallizations from isopropyl ether removed the unreacted diacetone glucose and gave fine needles of 3-*O*-carboxymethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose methyl ester, m.p. 104–105° C., $[\alpha]_D$ −3.5° (*c*, 1.5 in chloroform). Calc. for $C_{15}H_{24}O_8$: C, 54.2; H, 7.28; (OCH_3), 9.34%. Found: C, 54.4; H, 7.31; (OCH_3), 9.35%.

B. Method Using Sodium Hydride in Oil

Dispersed sodium hydride, 4 ml., was added to 5 gm. of 1,2;5,6-di-*O*-isopropylidene-D-glucofuranose in 75 ml. of absolute ethyl ether. The mixture was stirred in an atmosphere of dry nitrogen at room temperature for 18 hr. Methyl bromoacetate, 5 ml., was added, causing an immediate reaction with evolution of heat. Another 5 ml. of methyl bromoacetate was added after the mixture had been stirred at room temperature for 12 hr. After additional

stirring for 28 hr., 2 ml. of absolute methanol was added to decompose any excess of hydride, very little of which appeared to be left. Ethyl ether, 75 ml., and 50 ml. of water were added to the reaction mixture. The dark red aqueous layer formed was discarded and the ether layer was washed with four 25-ml. portions of water. The pale yellow ether solution was treated as above and yielded 8.3 gm. of a partially crystalline product (including 2.5 gm. of Bayol 85). Recrystallization from isopropyl ether gave 5.0 gm. in 78% yield of slightly colored needles, m.p. 103–104.5° C. Two more recrystallizations from the same solvent resulted in 4.2 gm. of a pure product with the same melting point and mixed melting point as the material referred to above.

Methyl 3-O-Carboxymethyl-α-D-glucopyranoside Methyl Ester

A sirup of 3-*O*-carboxymethyl-D-glucose (pure as indicated by paper chromatography), 0.93 gm., was dissolved in 75 ml. of 2.5% methanolic hydrogen chloride and 5 gm. of Drierite was added. The reaction mixture was kept at reflux temperature in a dry atmosphere for three days. The pale yellow solution was neutralized with silver carbonate and the cloudy filtrate obtained was clarified by saturating with hydrogen sulphide and heating. After filtering, the solution was concentrated *in vacuo* at 50° C. to a sirup, which was decolorized and clarified by dissolving in a small volume of methanol and treating with Darco G-60, three such treatments being necessary. The resulting sirup was dried *in vacuo* at 55° C. for two days and was found to weigh 0.82 gm. Although the product had the correct methoxyl analysis of 23.5% (theoretical 23.3%), it failed to crystallize after several months.

3-O-Carboxymethyl-D-glucose

A mixture of 7 gm. of 3-*O*-carboxymethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose methyl ester and 25 gm. of Amberlite IR-120 exchange resin in 25 ml. of water was stirred on a steam bath for 12 hr. The resin was filtered off and washed thoroughly with water. The combined filtrate and washings was treated with Darco G-60 and evaporated to approximately 50 ml. Freeze-drying of this solution gave 5.0 gm. of a friable resin-like material, $[\alpha]_D$ 51.2° (*c*, 1.5 in water), which was very hygroscopic. This product was chromatographically pure with regard to several solvent systems and several spraying agents. Other solutions of 3-*O*-carboxymethyl-D-glucose were evaporated to sirups which all failed to crystallize when subjected to various techniques used to induce crystallization. Calc. for $C_8H_{14}O_8$: C, 40.3; H, 5.9%. Found: C, 39.2; H, 6.0%. Titration of 64.0 mgm. in 5 ml. of water under nitrogen with 0.0222 *N* barium hydroxide and with methyl red as indicator resulted in the consumption of 12.66 ml. of barium hydroxide. This titer was equivalent to 66.9 mgm. of 3-*O*-carboxymethyl-D-glucose. Various techniques were applied to obtain sirups free of lactones, all of which, however, failed to produce the desired crystallization.

Methyl 3,5,6-Tri-O-benzyl-2-O-carboxymethyl-α,β-D-glucofuranoside Methyl Ester

Sirupy 3,5,6-tri-*O*-benzyl-α,β-D-glucofuranoside, 34 gm., was dissolved in 125 ml. of absolute ethyl ether. Dispersed sodium, 15 ml., was added dropwise

over a two-hour period with stirring and in an atmosphere of dry nitrogen, after which stirring was continued for six hours at room temperature. Methyl bromoacetate, 25 ml., was added dropwise and an exothermic reaction was observed. The mixture was stirred at room temperature for 12 hr. Water, 100 ml., and ethyl ether, 200 ml., were added to the gray reaction mixture, the color changing to red. The ether layer was washed with five 100-ml. portions of water, dried over sodium sulphate, and evaporated to 34 gm. of a light red sirup.

The product was dissolved in 100 ml. of tetrahydrofuran in a stainless steel bomb and 3 gm. of palladium black was added. Hydrogenation was effected at a pressure of 600 p.s.i. of hydrogen over a five-hour period and at 100° C. After the catalyst had been removed, 17.3 gm. of a brown sirup was obtained upon evaporation *in vacuo* of the filtrate. This material was stirred in 200 ml. of 2% sulphuric acid on a steam bath for eight hours. The hydrolyzate was extracted with eight 50-ml. portions of ethyl ether, evaporation of which yielded 4 gm. of a red, optically inactive sirup. The acid was neutralized with barium hydroxide and the barium sulphate digested on a steam bath for two hours. After centrifuging, the supernatant aqueous solution was slowly passed through a column of Amberlite IR-120 exchange resin and the latter washed with water until the effluent was neutral. Evaporation of the pale-yellow aqueous effluent *in vacuo* at 60° C. gave 9.0 gm. of a brown sirup. Paper chromatography showed a strong spot which was assigned to 2-*O*-carboxymethyl-D-glucose and a medium spot for glucose. After further purification with the aid of the same exchange resin, the final product contained only a trace of glucose.

Attempted Preparation of 2-O-Carboxymethyl-4,6-O-ethylidene-β-D-glucopyranoside 3-Nitrate Methyl Ester

Methyl 4,6-*O*-ethylidene-β-D-glucopyranoside 3-nitrate (7, 10), 1.6 gm., was stirred at room temperature under dry nitrogen with 2 ml. of dispersed sodium in 50 ml. of absolute ethyl ether for 20 hr. The orange-brown reaction mixture was cooled in an ice-bath and 10 ml. of methyl bromoacetate was added. The mixture was stirred at room temperature for one and one-half hours and at reflux for eight hours. Ethyl ether, 50 ml., was added and the ether solution was washed with three 50-ml. portions of water. The light yellow solution was dried over sodium sulphate and evaporated *in vacuo* at 40° and 90° C. to a yellow sirup weighing 0.6 gm. A spot test for organic nitrate with diphenylamine and sulphuric acid on the sirup was negative. Hydrolysis of a small amount of this material and paper chromatography indicated a strong spot for glucose and medium spots for the 2- and 3-*O*-carboxymethyl-D-glucoses and the 2,3-di-*O*-carboxymethyl-D-glucose.

6-O-Carboxymethyl-1,2;3,5-di-O-methylene-D-glucofuranose Methyl Ester

A. Method Involving Sodium Dispersed in Toluene

A solution of 1 gm. of 1,2;3,5-di-*O*-methylene-D-glucofuranose, prepared as described previously (14), in 25 ml. of absolute dioxane was treated with 2 ml. of dispersed sodium. The mixture was stirred in an atmosphere of nitrogen for

17 hr. and was then cooled in an ice-bath, after which 0.81 ml. of absolute methanol was added. The brown, gelatinous mixture was stirred for one hour at room temperature, methyl bromoacetate, 4.5 ml., was slowly added, and the resulting reaction mixture stirred for an additional four hours. Dioxane, 50 ml., was added and the mixture was centrifuged. The dioxane solution was concentrated *in vacuo* at 50° and 90° C. to a light red sirup, which was dissolved in benzene and applied to a column of 5:1 Magnesol–Celite. The latter was washed with 100:1 benzene–ethanol and the slightly yellow filtrate concentrated to a sirup weighing 1.15 gm. Hydrolysis and paper chromatography of a small amount of this material indicated a strong spot which was assigned to 6-*O*-carboxymethyl-D-glucose and a weak spot for glucose. The remainder of the sirup was rubbed on a watch glass with methanol and ethyl ether, crystallization occurring after 12 hr. A solution of 1.0 gm. of the sirup in 2 ml. of methanol was cooled, seeded, and allowed to crystallize at 5° C. A crystalline material in the form of long flat rods, 0.66 gm., corresponding to a yield of 49%, was obtained. The product had a melting point of 46.5–47.5° C. and $[\alpha]_D$ 32.7° (*c*, 1.3 in chloroform) after three recrystallizations from methanol at 5° C. Calc. for $C_{11}H_{16}O_8$: C, 47.8; H, 5.84; (OCH_3), 11.2%. Found: C, 47.7; H, 5.52; (OCH_3), 11.4%.

B. Method Involving Sodium Hydride

Dispersed sodium hydride, 2 ml., was added to a solution of 1,2;3,5-di-*O*-methylene-D-glucofuranose, 1.0 gm., in 25 ml. of absolute dioxane and the mixture was stirred under nitrogen for 25 hr. at room temperature. Methyl bromoacetate, 5 ml., was added and stirring continued for another 12 hr. After addition of 50 ml. of dioxane and centrifuging, the dioxane solution was evaporated to a sirup which was rinsed once with petroleum ether. Crystallization from methanol yielded 0.35 gm. in 26% yield of crystals with a melting point of 47–48° C. Paper chromatography after hydrolysis of the crude product showed a strong spot for 6-*O*-carboxymethyl-D-glucose and a weak spot for glucose.

C. Purdie Method

A mixture of 1.0 gm. of 1,2;3,5-di-*O*-methylene-D-glucofuranose, 2 ml. of methyl bromoacetate, 1.16 gm. of silver oxide, and a small amount of Drierite was stirred at 100° C. for two hours with exclusion of moisture. Another 0.5 gm. of silver oxide was added and the reaction was continued for another hour. Chloroform was added to the cooled mixture, followed by filtration. Evaporation of the filtrate *in vacuo* gave a sirup which was treated once more with the same reagents. The product was hydrolyzed and paper chromatography indicated spots of equal intensity for 6-*O*-carboxymethyl-D-glucose and glucose.

6-O-Carboxymethyl-D-glucose

A mixture of 2.8 gm. of 6-*O*-carboxymethyl-1,2;3,5-di-*O*-methylene-D-glucofuranose methyl ester and 6 gm. of Amberlite IR-120 exchange resin in 12 ml. of water was stirred at reflux temperature for 24 hr. The resin was removed by filtration and the filtrate clarified with Darco G-60. The sirup obtained after

evaporation *in vacuo* was carefully dried over phosphorus pentoxide and failed to crystallize after one month. The material was dissolved in water for easier handling and freeze-dried to a friable, resin-like material. Paper chromatography suggested the presence of only 6-*O*-carboxymethyl-D-glucose.

Methyl 4,6-O-Benzylidene-2,3-di-O-carboxymethyl-α-D-glucopyranoside Methyl Ester

Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (7), 3.0 gm., and 5 ml. of dispersed sodium hydride were stirred in 50 ml. of anhydrous dioxane at room temperature in an atmosphere of nitrogen for 13½ hr. The thick, gray, gelatinous reaction mixture was shaken with an additional 2 ml. of sodium hydride for another 61½ hr. Methyl bromoacetate, 10 ml., was added and the mixture stirred for 46 hr. After addition of 50 ml. of chloroform and centrifuging, the supernatant solution was evaporated *in vacuo* at 60° and 75° C. to a sirup, the Bayol was poured off, and the remaining material washed with petroleum ether to yield 7.8 gm. of a sirup. Hydrolysis of a small amount of the latter and paper chromatography indicated weak spots for glucose and 2-*O*-carboxymethyl-D-glucose and an additional, strong, faster moving spot which was assigned to 2,3-di-*O*-carboxymethyl-D-glucose. The sirup failed to crystallize after several weeks during which time it was subjected to various techniques for inducing crystallization.

A similar synthesis involving sodium dispersed in toluene yielded a product which, after hydrolysis and paper chromatography, showed strong spots for glucose and 2,3-di-*O*-carboxymethyl-D-glucose and somewhat weaker spots for the 2- and 3-*O*-carboxymethyl-D-glucoses.

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THE HEATS OF CRYSTALLIZATION OF VACUUM DEHYDRATED MAGNESIUM SULPHATE HEPTAHYDRATE AND COBALTOUS CHLORIDE HEXAHYDRATE[1]

By J. W. S. Jamieson[2] and G. B. Frost

ABSTRACT

Magnesium sulphate monohydrate prepared by vacuum dehydration of the heptahydrate does not yield a pattern of X-ray diffraction lines, and in this sense may be said to have an amorphous character. By measurement of the heats of solution of the "X-ray amorphous" and crystalline monohydrates, the heat of transition has been found to be 6550 cal. mole^{-1}. Cobaltous chloride monohydrate prepared by vacuum dehydration appears to be microcrystalline. The heat of transition to the normal crystalline form is 1390 cal. mole^{-1}. These values are related to the surface areas of the vacuum dehydrated products.

INTRODUCTION

Kohlschütter and Nitschmann (5) have shown that when copper sulphate pentahydrate is dehydrated under vacuum, a product of monohydrate composition is obtained which does not yield a pattern of diffraction lines on X-ray examination. Hammel (3) obtained similar results for other dimetal sulphates, and Volmer and Seydel (8) for manganous oxalate dihydrate. For convenience, the term "X-ray amorphous" will be used to designate such products. These products have high energy contents with reference to the corresponding crystalline salts. From measurements of heats of solution, Frost, Moon, and Tompkins (1) found values of the order of 7000 cal. mole^{-1} for the heats of transition from the "X-ray amorphous" to the crystalline forms of copper sulphate monohydrate and zinc sulphate monohydrate.

Wheeler and Frost (9) have shown that the vacuum dehydration of magnesium sulphate heptahydrate results in the gradual loss of water to the monohydrate stage, the product showing no X-ray diffraction lines. This product is very stable, the characteristic monohydrate (kieserite) lines being formed only when the product is heated for two days at 130° C. They also found that on vacuum dehydration of cobaltous chloride hexahydrate, a gradual loss in weight occurred, the rate being rapid to the dihydrate stage followed by a much slower rate. It was not possible to characterize the final product by X-ray diffraction using the radiation available.

In the course of a more comprehensive study of the dehydration kinetics of these salts, and of other studies, it became desirable to have reasonably accurate information concerning the energetic character of the products of monohydrate composition obtained by vacuum dehydration, in reference to the normally occurring crystalline monohydrates. The purpose of this paper is to report the results obtained.

EXPERIMENTAL

The experimental method involved the comparison of the heats of solution of the crystalline monohydrates with those of the products of stoichiometric

[1]*Manuscript received November 18, 1955.*
Contribution from the Department of Chemistry, Queen's University, Kingston, Ont.
[2]*Present address: Graduate student in Chemistry, McGill University, Montreal, Que*

monohydrate composition obtained by vacuum dehydration. The calorimeter and general procedures were identical with those described in detail in the earlier work on copper and zinc sulphates (1).

Magnesium sulphate heptahydrate and cobaltous chloride hexahydrate, both of reagent grade, were recrystallized twice at room temperature, air dried, and screened, the "through 60 on 80 mesh" fractions being retained.

A series of mixtures of crystalline hydrates were prepared by dehydrating small weighed samples for various times at 100° C. in an Abderhalden apparatus containing fused calcium chloride as a desiccant. The percentage of water in each sample was calculated from the loss in weight. The heats of solution of these samples were determined and plotted against the water content, the value corresponding to the monohydrate composition being determined by extrapolation.

Vacuum dehydration to various water contents was carried out as follows. A weighing thimble containing a small weighed sample was placed in a tube which was connected to a vacuum line by means of a ground joint. The system was then evacuated (usually at 40° C.) for a sufficient time to give a product of the approximate composition desired. At the end of the evacuation, the pump was shut off, and dry air admitted to the system. The sample container was then quickly removed, capped, and weighed, the water content being determined by the weight loss. The heats of solution of the samples were determined, plotted against water content, and the value corresponding to the stoichiometric monohydrate composition determined by interpolation.

Samples of the magnesium salt were characterized by X-ray diffraction as required. It was not possible to obtain suitable diffraction patterns with the cobalt salt using the copper K_α radiation available.

RESULTS

Magnesium Sulphate

The results of determinations of the heats of solution of pure magnesium sulphate heptahydrate and of crystalline mixtures of hydrates, prepared by the dehydration of the heptahydrate in the Abderhalden apparatus, are given in Table I. In this, and the following tables, the percentage of water in a given

TABLE I

HEATS OF SOLUTION OF CRYSTALLINE HYDRATES OF MAGNESIUM SULPHATE

Expt. No.	Per cent water $= c$	Heat evolved, cal. gm.$^{-1}$	Heat of dilution, cal. gm.$^{-1}$ hydrated salt	J, cal. gm.$^{-1}$ hydrated salt	Temp., ° C.
1	51.16	−14.16	2.44	−11.72	26.92
2	51.16	−13.47	1.82	−11.65	26.04
3	51.16	−13.51	2.04	−11.47	26.08
4	30.26	49.26	2.78	52.0	26.62
5	30.19	51.71	2.59	54.3	27.00
6	20.66	76.54	3.27	79.8	26.25
7	20.00	78.82	2.56	81.4	26.23

sample is denoted by c and the heat of solution to infinite dilution by J. Heats of dilution were obtained from the data of Lange and Streeck (6). The last column gives the temperature of the calorimeter at the instant of the salt addition. The results are plotted in Fig. 1, from which it will be seen that the

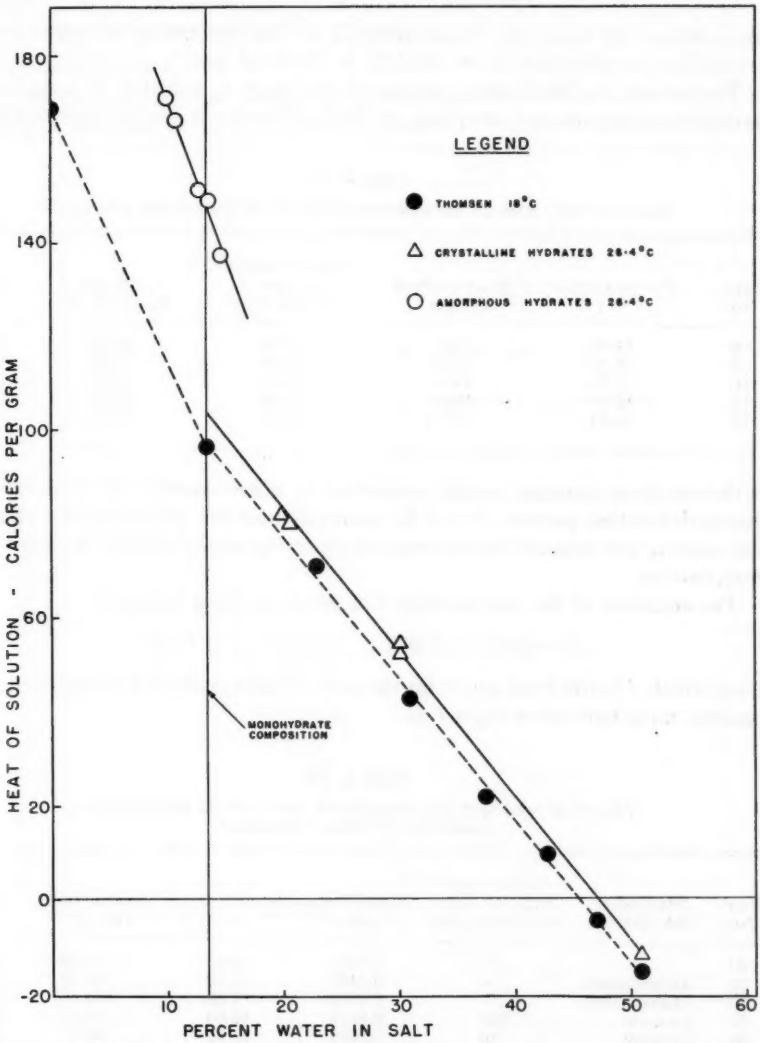

FIG. 1. Heats of solution to infinite dilution of crystalline and X-ray amorphous hydrates of magnesium sulphate.

heat of solution values for samples of water content between the heptahydrate and the monohydrate lie on a straight line.

The equation of the best straight line, fitted to the points obtained by the method of least squares, is

$$J = 142.8 - 3.012\,c \quad (13.02 < c < 51.16)$$

from which the value of J corresponding to the percentage of water in the crystalline monohydrate ($c = 13.02\%$) is 103.6 cal. gm.$^{-1}$.

The results for the determinations of the heats of solution of samples dehydrated under vacuum are given in Table II and are also plotted in Fig. 1.

TABLE II

HEATS OF SOLUTION OF AMORPHOUS HYDRATES OF MAGNESIUM SULPHATE

Expt. No.	Per cent water = c	Heat evolved, cal. gm.$^{-1}$	Heat of dilution, cal. gm.$^{-1}$ hydrated salt	J, cal. gm.$^{-1}$ hydrated salt	Temp., ° C.
8	14.68	132.7	3.78	136.5	26.53
9	13.69	144.5	3.45	148.0	26.31
10	12.79	147.4	3.35	150.8	26.23
11	10.81	162.4	3.38	165.7	26.84
12	10.04	167.4	3.21	170.7	25.97

Although these samples varied somewhat in water content, none showed an X-ray diffraction pattern. It will be observed that the values lie on a straight line cutting the vertical line corresponding to the stoichiometric monohydrate composition.

The equation of the best straight line fitted to these values is

$$J = 243.1 - 7.077\,c \quad (10.04 < c < 13.69)$$

from which J is 150.9 cal. gm.$^{-1}$ for the dehydration product having the stoichiometric monohydrate composition.

TABLE III

HEATS OF SOLUTION OF CRYSTALLINE AND VACUUM DEHYDRATED HYDRATES OF COBALT CHLORIDE

Expt. No.	Method of dehydration	Time of salt addition after evacuation, min.	Sample wt., gm.	Per cent water = c	Heat evolved, cal. gm.$^{-1}$	Temp., ° C.
20	—	—	2.3511	45.43	−8.32	25.93
21	Abderhalden	—	0.5188	11.99	94.08	25.46
22	Abderhalden	—	0.9115	7.69	110.4	26.45
23	Vacuum	359	0.5514	16.64	78.6	26.62
24	Vacuum	10	0.3988	16.92	81.1	25.73
25	Vacuum	10	0.3529	16.41	82.6	25.26
26	Vacuum	278	0.4820	16.92	78.6	25.92
27	Vacuum	122	0.4648	16.41	80.1	25.76
28	Vacuum	10.5	0.5944	18.50	71.0	26.30
29	Vacuum	10	0.3788	11.22	105.4	25.23
30	Vacuum	10	0.6225	8.62	119.3	25.94
31	Vacuum	130	0.4149	8.62	119.2	25.58
32	Vacuum	10	0.4995	3.09	147.7	25.51

The difference in these values of J is 47.3 cal. gm.$^{-1}$. Hence for:

$$MgSO_4.H_2O(\text{X-ray amorphous}) \rightarrow MgSO_4.H_2O(\text{crystalline}),$$
$$\Delta H_{300°K.} = -6550 \text{ cal. mole}^{-1}$$

with a probable uncertainty of ± 100 cal.

Cobaltous Chloride

The heat of solution results for both crystalline and vacuum dehydrated samples are given in Table III and are plotted in Fig. 2. Unfortunately no heat

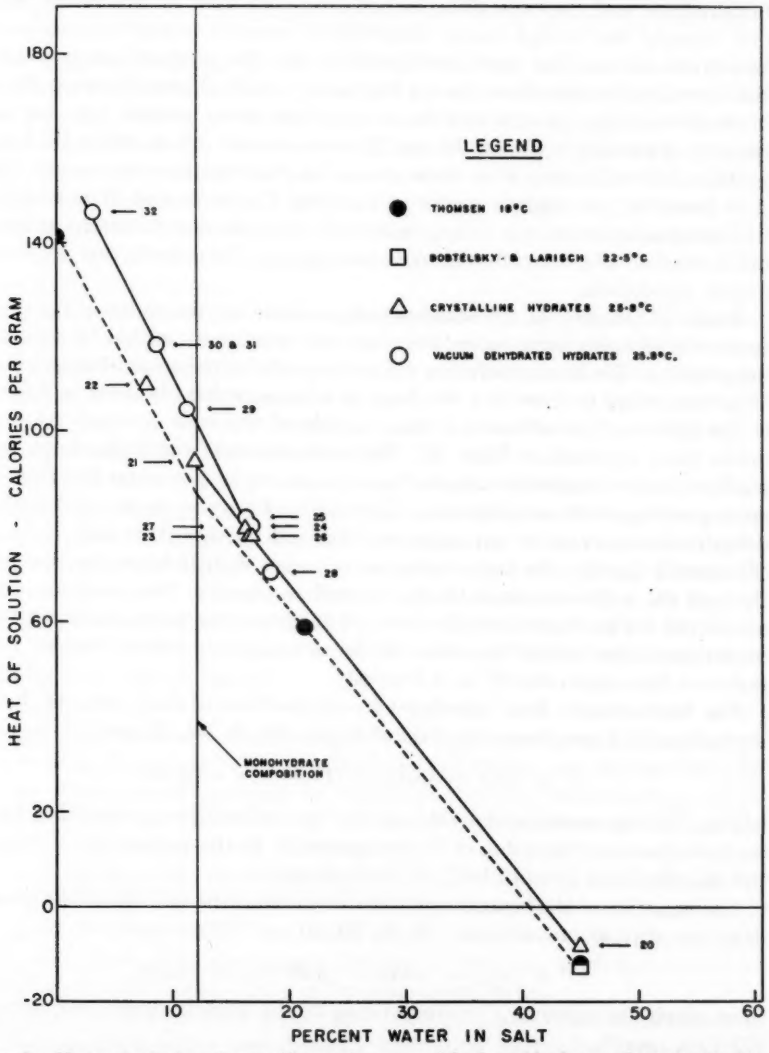

FIG. 2. Heats of solution of crystalline and vacuum dehydrated hydrates of cobalt chloride.

of dilution data are available for this salt. It has been thought desirable, therefore, to tabulate the sample weights used. The amount of water in the calorimeter in each determination was 591.6±0.2 gm.

The results obtained in Expt. 20 refer to the crystalline hexahydrate. In Expt. 21 dehydration was carried out to the crystalline monohydrate stage. Expt. 23 is a vacuum dehydration in which nearly six hours elapsed between the end of dehydration and the introduction of the sample into the calorimeter. It was observed that the heat of solution value for this vacuum dehydrated product fell on the straight line joining the values obtained for the crystalline hexahydrate and the crystalline monohydrate. In view of this result, it was first thought that a high energy intermediate was not formed on vacuum dehydration. It was then considered possible that the product had reverted to the normal crystalline form during the period which elapsed between the end of the dehydration process and the introduction of the sample into the calorimeter. Accordingly Expts. 24 and 25 were carried out in which the heat of solution determinations were made as soon as possible after evacuation. These were found to give slightly higher values than Expts. 26 and 27 in which dehydration was carried out to approximately the same water content as before, but a considerable time allowed to elapse between the dehydration and calorimetric procedures.

Expts. 29, 30, and 32 are vacuum dehydrations carried to lower water contents, the samples being introduced into the calorimeter within 10 min. after dehydration. The heat of solution values lie on the upper straight line of Fig. 2. It is interesting to note that the heat of solution value obtained in Expt. 30 is the same as that obtained from a sample of the same product taken two hours later, reported as Expt. 31. This indicates that the high energy intermediate is more stable for samples having a percentage of water less than that corresponding to the monohydrate. Expt. 28 is of interest in that, although the dehydration was carried out under vacuum and the sample transferred to the calorimeter quickly, the heat of solution value lies slightly below the line drawn through the values obtained for the crystalline samples. This result cannot be accounted for by experimental error and suggests that some phase transition occurs just prior to the formation of the monohydrate phase. Further exploration of this region would be of interest.

The best straight line, calculated by the method of least squares, for the crystalline hydrates, from the data of Expts. 20, 21, 23, 26, and 27 is:

$$J' = 130.1 - 3.048\,c \quad (11.99 < c < 45.43)$$

where J' is the experimental value of the heat of solution uncorrected for the heat of dilution. The value of J' corresponding to the percentage of water in the monohydrate ($c = 12.18\%$) is 93.0 cal. gm.$^{-1}$.

The equation of the best straight line for the heats of solution of the vacuum dehydrated products of Expts. 24, 25, 29, 30, and 32 was found to be

$$J' = 161.5 - 4.848\,c \quad (3.09 < c < 18.50)$$

from which the value of J' corresponding to the monohydrate composition is 102.4 cal. gm.$^{-1}$.

The difference in heat of solution between the vacuum dehydrated and crystalline monohydrates is therefore 9.4 cal. gm.$^{-1}$, or for the change in state,

$$CoCl_2.H_2O(\text{vacuum dehydrated}) \rightarrow CoCl_2.H_2O(\text{crystalline}),$$
$$\Delta H_{300°K.} = -1390 \text{ cal. mole}^{-1}.$$

This value is to be regarded as somewhat approximate in that the interval between evacuation and placing the sample in the calorimeter (during which some crystallization may have occurred in samples of higher water content) is arbitrary.

COMMENT

The value obtained in the foregoing for the heat of transition of X-ray amorphous magnesium sulphate monohydrate to the corresponding crystalline form is comparable to those previously reported for the copper and zinc sulphate monohydrates (1). The value obtained for the cobalt salt is significantly lower. It is unfortunate that characterization of the product obtained on vacuum dehydration could not be made by X-ray diffraction. However, such results would be of doubtful value in view of the rapidity of crystallization, unless a technique could be devised whereby dehydration could be carried out in the X-ray camera itself.

The surface area of magnesium sulphate monohydrate prepared by vacuum dehydration is approximately 8 meters^2 gm.$^{-1}$; that of cobalt chloride monohydrate is 35.9 meters^2 gm.$^{-1}$. Both of these values were determined by argon adsorption at 78° K. (7). The ratio of the heat of transition per gram to the surface area of the vacuum dehydrated product is 5.9 cal. meters^{-2} for the magnesium salt, and 0.26 cal. meters^{-2} for the cobalt salt.

Giauque (2) has reported a value of 22.2 cal. gm.$^{-1}$ for the heat of transition of magnesium oxide from a finely divided crystalline to the normal macrocrystalline form. Jura and Garland (4) have reported the surface area of finely divided magnesium oxide prepared in a similar manner to that of Giauque to be 86 meters^2 gm.$^{-1}$. The experimental evidence indicates that the heat of transition is wholly due to the difference in surface area between the finely divided and normal crystalline forms. The ratio of the heat of transition to surface area is 0.26 cal. meters^{-2}.

The identical agreement of this value with the ratio obtained for cobalt chloride is undoubtedly fortuitous in view of the uncertainties involved. Nevertheless, the values of these ratios are comparable, and suggest that the product of vacuum dehydration of cobaltous chloride hexahydrate is microcrystalline and that the difference in heat of solution between the normal crystalline monohydrate and that formed by vacuum dehydration results, as with magnesium oxide, from the difference in crystal dimensions only. If this view is correct, it must be assumed that the microcrystals are accessible to the gas used in determining the surface area by the usual adsorption methods, or, in other words, that the surface area values have the same significance for cobaltous chloride monohydrate as for magnesium oxide.

The vacuum dehydration products of both cobaltous chloride hexahydrate and magnesium sulphate heptahydrate have large internal surfaces resulting

from capillary formation (7). It is probable that these capillaries are formed as the lattice contracts with the movement of the dehydration interfaces along preferred planes. In terms of the foregoing interpretation, it must be assumed that, for the cobalt salt, this lattice contraction is associated with the formation of loosely packed aggregates of microcrystals differing from crystals of the normal monohydrate in dimensions only.

For magnesium sulphate monohydrate, prepared by vacuum dehydration, the ratio of heat of transition to surface area is very much higher. It is possible that this material also consists of microcrystals. If this is so, however, the dimensions of these must be below the limit required for X-ray diffraction (about 100 Å). It is possible that these crystallites are packed in localized regions and that the adsorption surface area gives, not the area of the microcrystals, but the area resulting from the internal capillary structure. Consequently, the ratio of heat of transition to surface area would have a very different meaning than that just considered.

It is of interest, however, to point out another aspect of the magnesium sulphate dehydration. The crystalline monohydrate (kieserite) is known to be very stable and does not lose water at temperatures below about 200° C. under atmospheric pressure. It has been suggested, on this basis, that the water molecule does not exist as an entity in the kieserite lattice. However, the data given in Table II show that a loss in weight, corresponding to water contents well below the monohydrate stage, takes place quite readily during vacuum dehydration at 40° C.

These products have been found to give the characteristic kieserite diffraction lines when heated for two or three days at about 130° C. It is possible, therefore, that vacuum dehydration of the heptahydrate results in the formation of an intermediate, which under proper conditions crystallizes into the kieserite lattice. The measured heat of transition would therefore be the energy release accompanying crystallization from the intermediate, and not that associated solely with change in surface.

It is intended to present other data pertinent to the nature of X-ray amorphous dehydration products in a later paper.

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THE LOW PRESSURE DEHYDRATION OF MAGNESIUM SULPHATE HEPTAHYDRATE AND COBALTOUS CHLORIDE HEXAHYDRATE[1]

By R. W. Ford[2] and G. B. Frost

ABSTRACT

Rates of dehydration under vacuum, and at a series of controlled water vapor pressures, have been carried out for powdered samples of magnesium sulphate heptahydrate and of cobaltous chloride hexahydrate. It has been found for the magnesium salt that as the pressures are increased, the rate at first drops rapidly, this decrease being followed by a period of acceleration which is followed in turn by a decline. The curves are similar to those previously reported for copper sulphate pentahydrate, but the changes occur over a much wider range of water vapor pressures. In the dehydration of cobaltous chloride hexahydrate the initial drop in rate with increase in water vapor pressure is not observed. The results are interpreted in terms of the crystallization of intermediate products in the presence of adsorbed water.

INTRODUCTION

Recently, Wheeler and Frost (8) have reported the results of a survey of the dehydration kinetics of a number of hydrated salts. It has been shown that the rate of dehydration is markedly affected by the pressure of water vapor at the reaction interface, acceleration in rate being frequently observed over certain pressure ranges. Some hydrated salts on low pressure dehydration yield products which do not give diffraction lines on X-ray examination and therefore have no evident crystalline structure. For others the end products are crystalline. A more detailed study of the rates of dehydration at a series of water vapor pressures of magnesium sulphate heptahydrate, and of cobaltous chloride hexahydrate, has revealed some interesting points, both of similarity and contrast, in these respects. The purpose of the present paper is to report these findings.

EXPERIMENTAL METHOD

Determinations of rates of dehydration under vacuum, and also at externally controlled and constant pressures of water vapor, have been carried out. The apparatus and experimental method differed in no important respect from that used by Frost and Campbell (2) in a comparable study of the dehydration kinetics of copper sulphate pentahydrate. Rates of dehydration were measured by reading the extension of a quartz spiral from which small powdered samples were suspended. Water vapor, at pressures below 4.58 mm., was obtained by maintaining ice crystals, deposited on glass wool, at suitable low temperatures. Water vapor at higher pressures was obtained by first evacuating the system containing ice crystals at low temperatures, and then allowing these to melt by surrounding the container with a temperature-controlled water bath through which cold water could be circulated as needed. It was found that the temperature could be controlled to $\pm 0.02°$ C.

[1]*Manuscript received November 18, 1955.*
Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario.
[2]*Present address: Graduate student in Chemistry, McMaster University, Hamilton, Ontario.*

In rate experiments carried out in the presence of water vapor, samples were nucleated by dehydrating under vacuum for two or three minutes during which period readings were taken. The spiral case was then shut off from the vacuum system and exposed to water vapor at the desired pressure, readings of spiral extensions being continued for the duration of the experiment. X-ray powder photographs were made of the dehydration products of magnesium sulphate heptahydrate. Unfortunately this was not possible for the cobalt salt since the copper K_α radiation used was strongly absorbed, resulting in fluorescent radiation.

RESULTS

Magnesium Sulphate Heptahydrate

The dehydration of magnesium sulphate heptahydrate was studied at 40°, 50°, and 60° C. and over a range of water vapor pressures from zero to approximately 18 mm. Hg at each temperature. At 40° C., eight experiments were conducted, curves showing loss in weight in milligrams versus time in minutes being shown in Fig. 1.

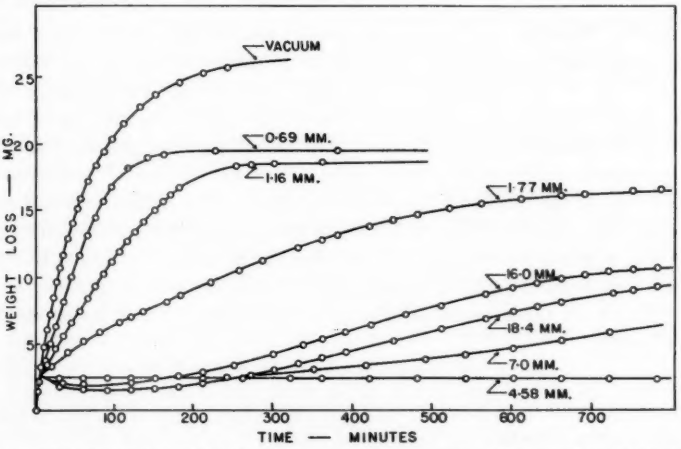

FIG. 1. The change in weight loss of fine crystal aggregates of magnesium sulphate heptahydrate at a series of constant water vapor pressures at 40° C.

These curves fall into three groups. Under vacuum, and at water vapor pressures of 0.69, 1.16, and 1.77 mm., the curves show a smooth and gradual decrease in rate as the dehydration progresses. Also the initial slope of each curve decreases with increasing pressure. The composition of the products varied from the monohydrate in the vacuum dehydration to approximately the tetrahydrate stage in the dehydration at 1.77 mm. None of these products diffracted X-rays.

The curve obtained at 4.58 mm. was unique in that no decomposition was apparent after the initial nucleation period.

All of the experiments at pressures of 7 mm., or higher, gave curves of a sigmoid character; that is, following nucleation, an induction period set in

during which no weight loss was observed. During this period, a slight gain in weight was sometimes noted, which was probably due to the adsorption of water on the outer dehydrated layer. This period was followed by another during which the rate of decomposition was almost constant with time, before gradually decreasing as the reaction neared completion. It will be seen that for the curves obtained at 7.0 mm., 16.0 mm., and 18.4 mm., the slopes of these nearly linear portions first increase with increasing pressure and then decline. The end products corresponding to these sigmoid type curves were crystalline, clearly defined diffraction patterns of tetrahydrate lines being obtained.

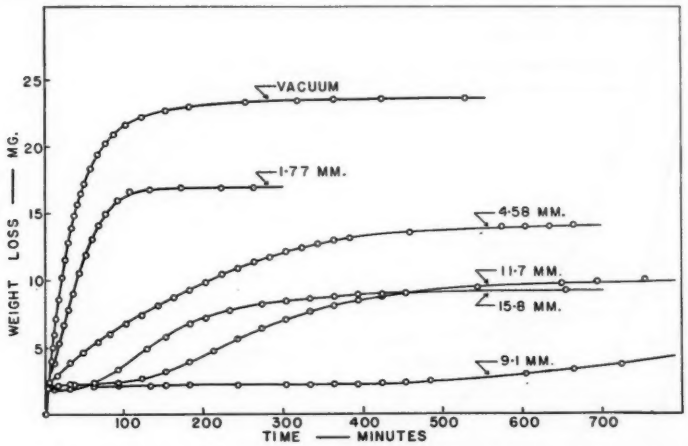

FIG. 2. The change in weight loss of fine crystal aggregates of magnesium sulphate heptahydrate at a series of constant water vapor pressures at 50° C.

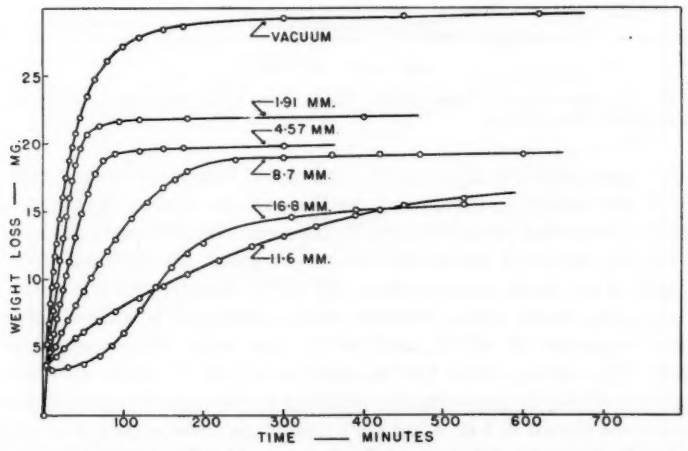

FIG. 3. The change in weight loss of fine crystal aggregates of magnesium sulphate heptahydrate at a series of constant water vapor pressures at 60° C.

Curves obtained from dehydrations carried out at 50° C. and 60° C. are shown in Figs. 2 and 3 and are similar in character to those just described.

It is evident from all of these plots that the duration of the induction periods decreases as either the pressure or the temperature is increased. This effect of pressure is shown most clearly in the group of curves obtained at 50° C.

The change in rate of dehydration with water vapor pressure per decigram of material is shown in Fig. 4. These rates have been obtained by the method used by Frost and Campbell (2) in their study of the dehydration of copper

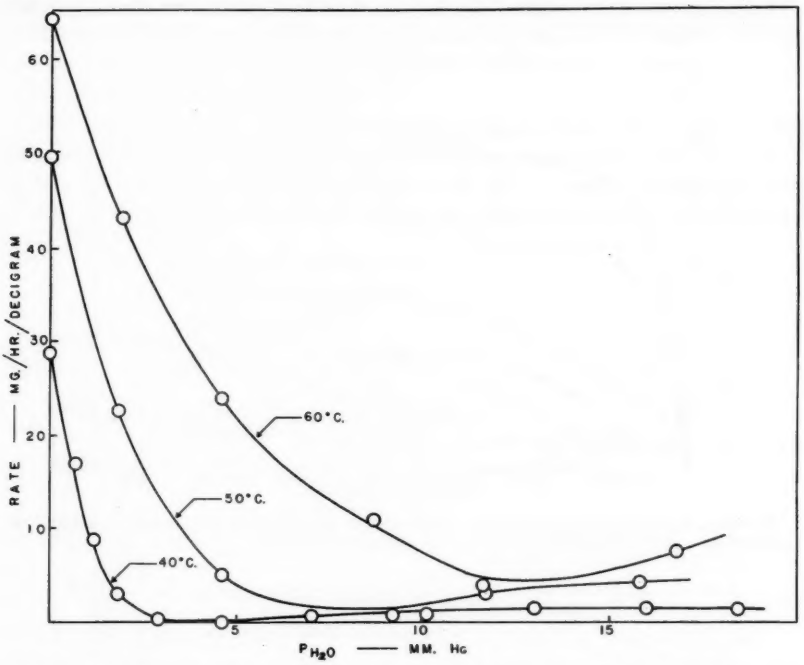

FIG. 4. The dependence of over-all dehydration rate upon water vapor pressure for magnesium sulphate heptahydrate.

sulphate pentahydrate. Essentially, the rates compared correspond to the slopes of the initial (nearly linear) portions of the curves showing a gradual decline in rate at low pressures, and to the slopes of the nearly linear portions following the induction period for the curves which are sigmoid in character.

At each of the three temperatures, the rate is seen to decrease fairly rapidly with increasing water vapor pressure until a minimum is reached, after which the rate increases. At 40° C., and 50° C., the rates decline again at higher pressure. This decline could not be observed at 60° C. since sufficiently high pressures could not be conveniently obtained by the experimental method used.

The curves shown in Fig. 4 are very similar to these reported by Frost and Campbell for copper sulphate pentahydrate, and by Topley and Smith (5) and

by Volmer and Seydel (6) for manganous oxalate dihydrate, except that the pressure at which the minimum in rate occurs is very much higher. The minimum occurs at higher pressures as the temperature is increased.

Cobaltous Chloride Hexahydrate

Studies of the rate of dehydration of this salt were carried out at 30° C. and 40° C. at water vapor pressures ranging from zero to approximately 18 mm. Hg.

The dehydration curves obtained at these two temperatures are shown in Figs. 5 and 6 respectively. The end product of the vacuum dehydrations, which were carried out for 30 hr., was a product of somewhat lower water content

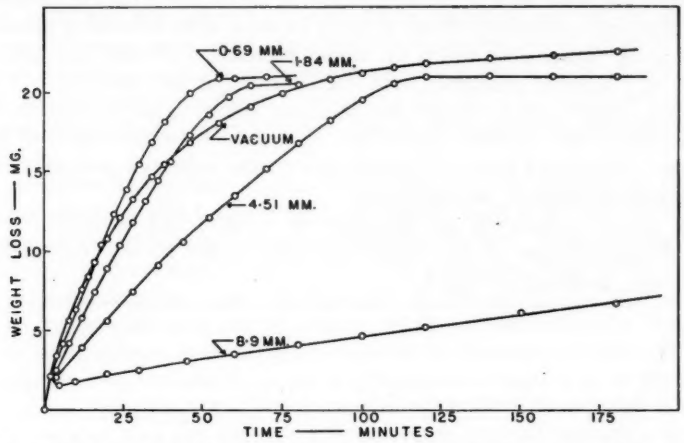

FIG. 5. The change in weight loss of cobalt chloride hexahydrate at a series of constant water vapor pressures at 30° C.

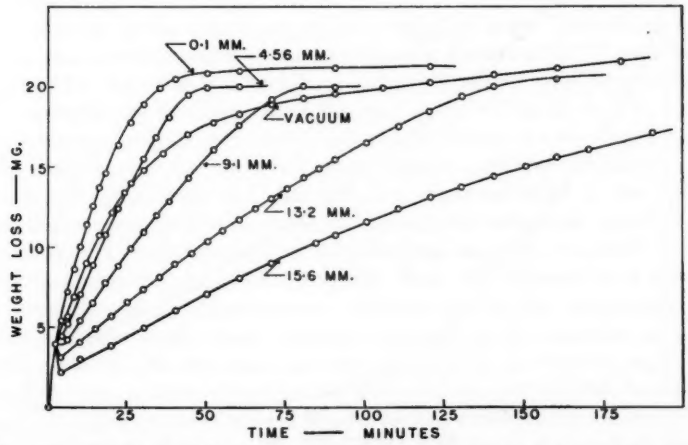

FIG. 6. The change in weight loss of cobalt chloride hexahydrate at a series of constant water vapor pressures at 40° C.

than the stoichiometric monohydrate composition. For the other determinations, the rate of decomposition became very slow when the dihydrate stage was reached. Control experiments showed that no significant amount of hydrogen chloride was formed in any of these dehydrations (4).

These curves show several interesting features in comparison with those obtained for magnesium sulphate heptahydrate. The curves obtained for vacuum dehydrations are somewhat similar. However, when water vapor at low pressure is admitted to the system, the cobalt salt shows quite different properties. Whereas with the magnesium salt, the initial slopes of the weight-loss curves decrease with increasing pressure, the slopes of the curves obtained with cobalt chloride hexahydrate initially increase with increasing pressure up to a limiting value, after which the slopes decrease, and then only gradually. Curves of a sigmoid character were not obtained at any pressure. At higher pressures, a slight gain in weight was observed following the nucleation period, but this effect was probably due to the adsorption of water vapor on the dehydrated surface and bore no resemblance to the induction periods observed for magnesium sulphate heptahydrate.

Rate values, calculated per decigram of sample, and obtained from the nearly linear portions of the weight-loss curves, are shown plotted against water vapor pressure in Fig. 7.

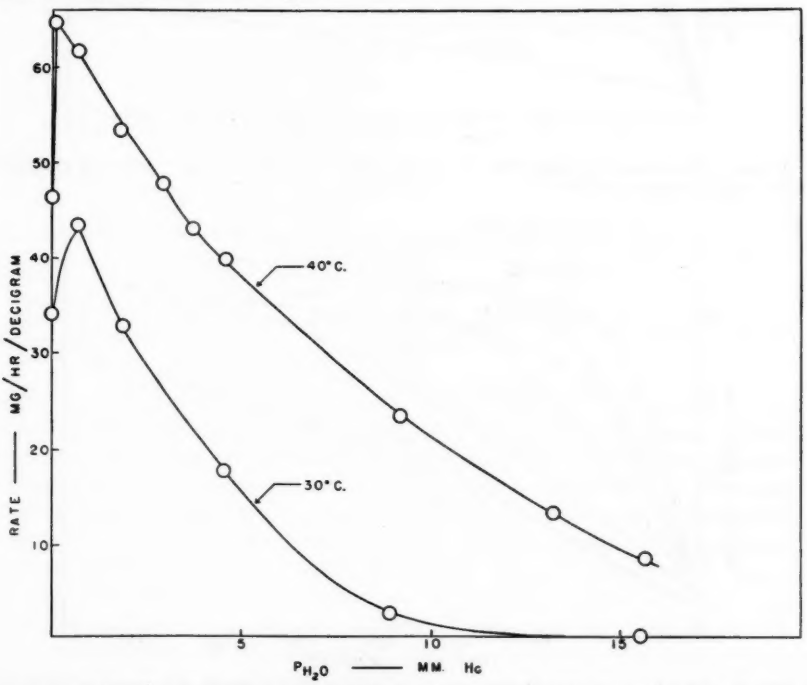

FIG. 7. The dependence of over-all dehydration rate upon water vapor pressure for cobalt chloride hexahydrate.

DISCUSSION

The dependence of the rate of dehydration of magnesium sulphate heptahydrate upon water vapor pressure has been found to be similar to that which has been reported for copper sulphate pentahydrate except that the minimum in rate occurs in a very much higher range of pressure. It would appear reasonable therefore to give the same interpretation of these curves as has been done for the copper sulphate pentahydrate dehydration (2). Under vacuum, the parent lattice breaks down into a state of monohydrate composition which does not yield a pattern of X-ray diffraction lines. It has been shown elsewhere that this material is very stable, and that the heat of crystallization is approximately 6500 cal. per formula wt. (3). Data regarding its surface area and capillary structure have been reported (4). At water vapor pressures below those corresponding to the minima in rates shown in Fig. 4, a material is formed which likewise does not diffract X-rays, but the rate of dehydration becomes very slow after the approximate stoichiometric composition of the tetrahydrate is reached.

At pressures higher than those corresponding to the minima in rates (or therefore those for which the weight loss curves show induction periods) the end product of dehydration is crystalline tetrahydrate. In these experiments a layer of amorphous material is formed in the nucleation stage of dehydration. Upon exposure to water vapor the induction period immediately sets in, which may be interpreted as a period during which crystallization of the X-ray amorphous transition layer takes place under the influence of adsorbed water. This effect occurs over small ranges of pressure and appears to be specifically due to water. Experiments have been carried out in order to ascertain if methyl or ethyl alcohol have any effect in accelerating the rate of these dehydrations, but with negative results. Upon the occurrence of crystallization the escape of water molecules is facilitated, giving rise to the nearly linear increase in the loss-in-weight curves following the induction periods. The final decline in rate may be ascribed to the impedance of this crystalline layer. The occurrence of a zero rate at approximately 4.58 mm. in the dehydration at 40° C. is of interest. It is probable that this is a very long induction period, and if carried farther would resemble the dehydration of 9.1 mm. at 50° C. shown in Fig. 2.

The relatively high pressure at which the minimum in rate occurs has been related elsewhere to the low adsorptive capacity and the capillary structure of the X-ray amorphous material (4). The observed shift of the minimum toward higher pressures by increase in temperature would be expected if it is assumed that a definite quantity of adsorbed water is required to induce crystallization of the amorphous material. Since the adsorption of water will be lowered by rise in temperature, it follows that as the temperature is increased, a higher water vapor pressure external to the interface will be required to provide the necessary quantity of water in the reaction zone.

The dependence of the rate of dehydration of cobaltous chloride hexahydrate upon water vapor pressure is very similar to that observed for the dehydration of chrome alum by Cooper and Garner (1) who made microscopic measurements on the rate of growth of nuclei on single crystals. They assumed the

formation of a transition layer (probably microcrystalline) at the reaction interface and explained the maximum in rate observed at low pressure as being due to a decrease in the thickness of this transition layer as a consequence of the development of macrocrystals of the product. X-ray powder photographs, made in this laboratory, of the vacuum dehydration product of chrome alum show a definite diffraction pattern. Although X-ray diffraction data for the cobalt salt are lacking, observations reported by Jamieson and Frost (3) during determinations of the heat of solution of the vacuum dehydrated product indicate that vacuum dehydration results in a microcrystalline product of high internal surface, the formation of macrocrystals occurring readily.

The group of loss-in-weight versus time curves obtained for this salt are similar to the group of curves following the long induction periods observed in the dehydration of magnesium sulphate heptahydrate or copper sulphate pentahydrate, in that the over-all dehydration rate at first increases with water vapor pressure, and then declines. The absence of observable induction periods in the dehydration of cobalt chloride hexahydrate suggests that the processes assumed to occur during them (i.e. crystallization of amorphous material) either do not occur at all, or take place at extremely low pressures.

It is possible that a state corresponding to the X-ray amorphous state of magnesium sulphate monohydrate is formed as a transitory step as the primary lattice breaks down, but that crystallization occurs immediately. If the presence of water is a necessary factor, this crystallization must take place merely as water molecules from the reaction zone pass through the transition layer. There will result a mesh of microcrystals interspersed with capillaries formed by lattice contraction, the surface properties of which have been described elsewhere (4).

With increase in water vapor pressure external to the reaction zone, further adsorption will occur, resulting in crystal growth, and further contraction in volume, resulting in larger capillaries. In consequence, the more rapid escape of water molecules from the reaction interface will be facilitated, and the observed increase in rate accounted for. The decline in rate following the observed maximum may, as before, be ascribed to the impedance of the growing crystalline layer. This crystalline layer appears to have the composition of the dihydrate. It has been pointed out elsewhere (8) that the rate of dehydration under vacuum proceeds fairly rapidly to the dihydrate stage, followed by monohydrate formation at a slower rate. It appears that this second rate becomes very much slower in the presence of water vapor at low pressures.

It should be noted that the maximum in rate is displaced in the direction of lower pressure with temperature increase, whereas the reverse is true for magnesium sulphate heptahydrate. It has been pointed out that if water plays any significant role in the formation of crystalline dehydration products of cobalt chloride hexahydrate, the quantities required are very small. Any slight adsorption of water will of course decrease with temperature rise. However, it has been shown (3) that the product formed on vacuum dehydration forms

macrocrystals very readily. It is probable that this crystallization rate increases with temperature and is therefore more significant than the adsorption factor.

In this study, and in other studies of the rates of dehydration of hydrated salts which have been reported, there seems to be a common over-all pattern of the sequence of changes occurring. The point of real interest is the mechanism whereby these changes occur in the presence of adsorbed water, and the variation in the range of pressures of water vapor over which this sequence of changes is observed for different salts. It would be of interest to attempt to correlate these findings with data concerning the crystallographic changes involved. Although some suggestive information is available concerning these crystal structures (7), our knowledge is not as yet sufficiently comprehensive for this purpose.

ACKNOWLEDGMENTS

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THE INFLUENCE OF ALKALI ON THE OXIDATION OF TETRALIN[1]

By K. U. Ingold

ABSTRACT

Strong alkalies are powerful catalysts for the initial oxidation of tetralin but their catalytic activity is rapidly replaced by an inhibiting action which makes oxidation of more than 5% of the tetralin an exceedingly slow process. Inhibition is due to the base catalyzed enolization and oxidation of the initial product, 1-tetralone, to various naphtholic compounds. Ring scission yields β-2-carboxyphenylpropionic acid. The rate shows a certain periodicity which may be due to the reaction proceeding by a series of consecutive autocatalytic steps.

INTRODUCTION

Not much is known about the influence of alkali on the oxidation of liquid hydrocarbons (4) but some recent work in these laboratories has shown that the rate of oxidative discoloration of lubricating oils is markedly reduced by the addition of alkali (17). The present work was started in the hope of elucidating this effect by the examination of a less complex system.

Tetralin was chosen for study as a large amount of work has been done on its catalyzed, uncatalyzed, and inhibited oxidation (1, 6–10, 13, 15, 16). The general features of its oxidation are now fairly well understood. In the uncatalyzed reaction tetralin is autoxidized first to a fairly stable hydroperoxide which subsequently breaks down to give a variety of products (16).

EXPERIMENTAL

The general design of the apparatus was the same as that described by Cooper and Melville (3). The manostat, which was used to follow the oxygen uptake at constant pressure, was immersed in a water bath at 34.0° C. The pyrex reaction vessel was connected to the manostat by way of a silicone greased cone and socket and a flexible glass spiral. The cone had a short projection on it that prevented any tetralin which distilled up to the grease during the course of a reaction from returning to the reactants. The reaction vessel was immersed in an oil bath at 119.0° C. and was shaken at 250 cycles/min. Tetralin was added to it from a constant volume pipette (3) which delivered 2.5 ml. The reaction vessel was cleaned by washing with benzene, alcohol, and distilled water, followed by heating to the softening point of glass in a stream of dry air in order to burn out any insoluble residue.

Infrared spectra were taken with a Model 21 Perkin–Elmer infrared spectrophotometer.

PURIFICATION OF TETRALIN

Commercial tetralin was shaken repeatedly with concentrated sulphuric acid until there was no discoloration. It was then washed with water, dilute alkali, and again with water. After being dried with $CaSO_4$ it was run through

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an alumina column and distilled twice under vacuum from sodium through a 2 ft. column packed with Dixon gauze rings (2). It was stored under an atmosphere of pure nitrogen.

Infrared analysis showed the purified tetralin to contain less than 0.05% of hydroperoxide, less than 0.1% of ketone, and only a very small amount of 1,2-dihydronaphthalene. The refractive index was 1.538_8 (n_{25}^{D}).

RESULTS

Kinetic Data

All the work reported in this paper was done at 119.0° C. with 2.5 ml. samples of tetralin.

Table I gives some data on the effect of various alkaline additives on the maximum rate of oxidation of tetralin (r_{max}, given in ml. O_2 at S.T.P./liter

TABLE I

EFFECT OF ALKALI ON THE OXIDATION OF TETRALIN

Additive	r_{max}	t_{max}	t_1	t_3	t_5	t_6	t_{10}	t_{20}
None	12.9	2550	560	990	1295	1425	1865	2855
Strong alkali	20.0	275	265	590	1630	3270	11800	23000 (t_{12})
0.5 gm. Na_3PO_4	9.9	75	160	565	885	1035	1565	2875
	9.8	1700						
1.0 gm. $C_6H_4(CO_2)_2K_2$	10.9	2100	550	950	1240	1380	1870	—
0.1 gm. Na_3PO_4	12.4	2500	520	970	1275	1415	1875	2950
2.0 gm. Na_3PO_4	18.1	75	75	415	1200	1690	3445	7400
Clear liquid from "alkali" run	10.2	2300	430	890	1210	1360	1910	3200

tetralin/sec.), on the time at which the maximum rate is reached (t_{max}, sec.), and on the times to various percentages of oxidation (t_1, t_3, etc., calculated for 1 mole O_2/mole tetralin). All data given are averages of at least two experiments. The run without additives, called hereafter the "normal" run, was an average of about 20 runs, none of which differed by more than 5% from the mean. In the presence of strong alkali, although the time taken to reach a given amount of oxidation was reproducible to within 5 or 10%, the maximum rate was of such short duration that it may be in error by 20%. Within the experimental error the same rates and times were obtained with 0.1–0.5 gm. NaOH, 0.5 gm. of sodium metal, and 0.5 gm. of a 10% Na – 90% Pb alloy. These runs with strong alkali are called hereafter "alkali" runs. For contrast the "normal" and "alkali" oxidation curves are shown in Fig. 1. It can be seen that the initial catalytic activity of the alkali is rapidly replaced by a strong inhibiting action. In addition to the very sharp maximum at 275 sec., there are two or more subsidiary maxima, the most noticeable of which occur at about 650 and 1300 sec.

The "normal" reaction went through the color sequence from light yellow (10% oxidation) to canary yellow (35%) and finally to a viscous reddish-orange oil. Oxidation in the presence of strong alkali gave a fine suspension of solid particles which went through a large range of colors. At 5% oxidation the color was yellow, at 7% brown, then greenish-brown, green (9%), dirty green, yellow,

and finally reddish-orange (10–12%). If the suspension was removed by centrifuging or by extraction with water, the liquid remained colorless until about 10% oxidation; it then showed a faint reddish-yellow color.

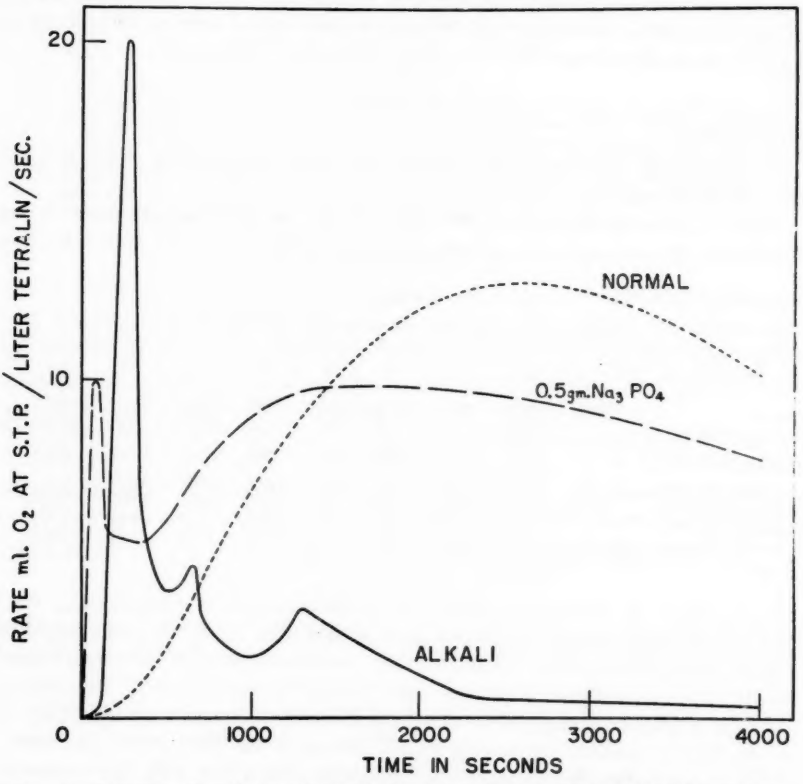

FIG. 1. The rates of oxidation of tetralin for "normal", "alkali", and Na_3PO_4 reaction.

The effect of moderate amounts of weak alkali, e.g. 0.5 gm. of dehydrated Na_3PO_4, was to give a combination of the "normal" and the "alkali" oxidation curves. The curve showed two maxima, the first near the beginning of the reaction and the second at about 12% oxidation (see Table I and Fig. 1). The liquid was a faint reddish-yellow at 30% oxidation.

Small amounts of weak alkali, e.g. 0.1 gm. of Na_3PO_4, or larger amounts of very weak alkali, e.g. 1.0 gm. of dipotassium phthalate, merely lowered the maximum rate of an otherwise "normal" reaction. The liquid was canary yellow at 25% oxidation.

Large amounts of weak alkali, e.g. 2 gm. of Na_3PO_4, gave an oxidation curve of the "alkali" type. However, the rate after 6% oxidation did not decrease sharply, but steadied down to a value of about 3.0 after 600 sec. The liquid was reddish-yellow at 25% oxidation.

A 5% oxidized "alkali" run (rate = 0.4) was centrifuged and all the solids removed. Measurements were then made on the further oxidation of the clear liquid (Table I). The reaction was of the "normal" type with only slight inhibition. The liquid became light yellow in color. The solid portion of the "alkali" run was washed with tetralin, dried, and then added to a fresh sample of tetralin. The rate remained low (0.38) and fairly constant to 12,000 sec. (t_1 = 4,800, t_3 = 11,700 sec.). The liquid remained colorless.

The addition of 0.3 gm. NaOH to a "normal" run after 1500 sec. (rate = 10.0) produced for the first 50 sec. an apparent negative rate due to the evolution of steam. After 400 sec. the rate reached its maximum value (3.9) and then fell rapidly to a low value characteristic of an "alkali" reaction. The pale yellow color of the "normal" run was changed to a pale pink. Na_3PO_4 would also convert the yellow color of a "normal" run to the pale pink color characteristic of an "alkali" run.

It is known from the work of Hock and Susemihl (11) that 1-tetralone is a major product of the "alkali" reaction. The influence of pure 1-tetralone on the oxidation of tetralin was therefore studied.

The addition of 0.2 ml. of 1-tetralone had only a slight effect on the reaction. The oxidation times were the same as those of a "normal" run but the maximum rate was a little lower (Table II). A rather larger inhibition was obtained by the addition of 0.2 ml. of a sample of 1-tetralone which had been 3% oxidized.

TABLE II

EFFECT OF KETONES ON THE OXIDATION OF TETRALIN

Additive	r_{max}	t_{max}	t_1	t_2	t_5	t_{10}	t_{20}
0.2 ml. 1-tetralone	12.2	2600	555	980	1285	1895	2950
As above, 3% oxidized	10.1	3900	590	1190	1625	2430	3760
0.5 ml. 1-tetralone + 0.3 gm. NaOH	4.6	2250	950	1630	2190	3740	—
0.2 ml. *n*-valerophenone	12.6	150	110	330	540	1045	2105

1-Tetralone autoxidized very slowly compared with tetralin, but in the presence of alkali it was oxidized to a dark viscous oil with extreme rapidity, the rate reaching 78.0 in 300 sec. A large amount of water was evolved and the reaction mixture went rapidly through the color sequence blue-green, brown-green, brown, purple, cherry red, and finally black and opaque. In contrast a mixture of 1-tetralone, tetralin, and alkali gave a "normal" type oxidation curve with a very low maximum rate (Table II). The liquid became cherry red in color.

For comparison with the effects produced by 1-tetralone some experiments were done adding other compounds containing a carbonyl group adjacent to a benzene ring.

The addition of 0.1 ml. of acetophenone gave a slightly lower maximum rate than a "normal" reaction, but the same amount had no effect on the reaction in the presence of strong alkali.

The addition of 0.2 ml. of *n*-valerophenone ($C_6H_5.CO(CH_2)_3CH_3$) strongly catalyzed the oxidation of tetralin (Table II). Within the first 200 sec. the

rate rose to the maximum value characteristic of the "normal" rate of oxidation. It then decreased in accordance with first order kinetics until 20% of the tetralin had been oxidized. Beyond 20% the rate decreased more rapidly.

n-Valerophenone autoxidized very slowly ($r = 0.4$ after one hour, 0.45% oxidized); its rate of oxidation at 119° C. was unaffected by alkali. The addition of *n*-valerophenone and alkali to tetralin (Table III) gave an "alkali" type

TABLE III

EFFECT OF *n*-VALEROPHENONE (V) AND ALKALI ON THE OXIDATION OF TETRALIN

Additive	r_{max}	t_{max}	t_1	t_3	t_5
0.1 ml. V + 0.1 gm. NaOH	18.8	180	210	670	1325
2.0 ml. V + 0.1 gm. NaOH	15.0	310	230	400	1190
2.0 ml. V + 0.2 gm. NaOH	10.5	230	250	555	1170
As above, oxidized 0.2%	1.6	500	3200	—	—
2.0 ml. V + 0.5 gm. NaOH	8.9	225	350	6000	—

curve but with the maximum rate dependent on the amount of alkali and to a lesser extent on the amount of ketone. The addition of a partially oxidized (0.2%) mixture of 2 ml. of *n*-valerophenone and 0.2 gm. NaOH to tetralin gave a strongly inhibited "alkali" curve (Table III).

A few experiments were also done on the oxidation of tetralin in the presence of *n*-valerophenone and weak acids (Table IV).

TABLE IV

EFFECT OF *n*-VALEROPHENONE (V) AND ACID ON THE OXIDATION OF TETRALIN

Additive	r_{max}	t_{max}	t_1	t_3	t_5	t_{10}	t_{20}
0.5 gm. $C_6H_4(CO_2)_2KH$	12.4	2300	510	900	1190	1775	2840
0.5 gm. $C_6H_4(CO_2)_2KH$ + 0.2 ml. V	11.5	2050	260	575	830	1410	2535
0.5 gm. $C_6H_4(CO_2)_2H_2$	11.2	2450	570	1005	1320	1940	3120
0.5 gm. $C_6H_4(CO_2)_2H_2$ + 0.2 ml. V	11.6	2300	740	1150	1435	2010	3170

The addition of 0.1 ml. of commercial benzaldehyde increased the rate of the "normal" oxidation, but it decreased the rate of the "alkali" reaction. Benzyl alcohol reduced the rate of both "normal" and "alkali" reactions.

The addition, at the beginning of a run, of phenolic compounds such as 2-naphthol, sodium salicylate, γ-2-hydroxyphenylbutyric acid and its sodium salt almost completely inhibited the oxidation of tetralin. Their addition in the middle of a run caused a marked reduction of rate, e.g. 0.1 gm. of γ-2-hydroxyphenylbutyric acid when added to a "normal" run after 1300 sec. caused the rate to drop from 8.8 to 1.1 (cf. 16).

Dehydrating agents such as $CaSO_4$, P_2O_5, and conc. H_2SO_4 completely inhibited the oxidation of tetralin for at least 5000 sec.

Analysis for Products

The infrared spectrum of pure tetralin was compared with the spectra of the products of the "normal" and "alkali" reactions. The "normal" runs showed

one strong new band at 3470 cm.$^{-1}$ due to O—H stretching in the hydroperoxide. With increasing oxidation hydrogen bonding caused this band to become broader and its maximum to shift to lower wave numbers. There were also some new but weaker bands at lower wave numbers (830, 880, and 912 cm.$^{-1}$) which can also presumably be associated with the hydroperoxide group.

The "alkali" runs showed a number of weak bands and one strong new band at 1683 cm.$^{-1}$ due to C=O stretching. There were no bands due to hydroperoxide, but instead a weak band appeared at 3550 cm.$^{-1}$ which may be due to a naphtholic OH group.

The spectrum of pure 1-tetralone gave a strong band at 1683 cm.$^{-1}$ and a number of weaker bands at lower wave numbers which accounted for most of the differences between the tetralin and "alkali" spectra. For runs lasting less than 6000 sec., i.e. less than about 8% oxidation, the intensity of the 1683 cm.$^{-1}$ band was roughly proportional to the amount of oxidation, but for longer runs its intensity was very much reduced. At 12% oxidation (23,000 sec.) the 1683 band corresponded to only about 2% oxidation, i.e. to about one sixth of the products; since no other new bands appeared the end products of the "alkali" reaction must be rather insoluble in tetralin. Acidification of an "alkali" run eliminated a weak band at 1560 cm.$^{-1}$, but two new bands appeared at 1728 cm.$^{-1}$ and 1715 cm.$^{-1}$. This represents the change from ionized to non-ionized carboxylic acids. The reverse of this process was observed when alkali was added to the products of a "normal" run, i.e. two weak bands at 1728 cm.$^{-1}$ and 1715 cm.$^{-1}$ were replaced by a band at 1560 cm.$^{-1}$. β-2-Carboxyphenylpropionic acid (see below) gave a strong band at 1728 cm.$^{-1}$. The carboxylic acid band at 1715 cm.$^{-1}$ was not characterized.

When alkali was added to the end product of a "normal" run the hydroperoxide was destroyed. Its addition at 6% oxidation gave only 1-tetralone but at 12% a weak new band appeared at 1670 cm.$^{-1}$ which became stronger than the 1683 cm.$^{-1}$ band at 35% oxidation. This band did not appear in the "alkali" reaction. It is probably due to a naphthoquinone.

No other differences of any magnitude were noted in the spectra.

The orange suspension from a 12% oxidized "alkali" run dissolved in water to give a red solution. On acidification the solution turned faint yellow and an acidic, slightly soluble orange oil was obtained. This oil was recrystallized twice from methyl alcohol and identified as 2-hydroxy-1,4-naphthoquinone (m.p. 189° C. (decomp.) (18)).

The green compound was not isolated from an "alkali" run. It was obtained by adding sodium hydroxide to a 12% oxidized "normal" run and heating the mixture at 119° C. for 15 min. The sodium hydroxide pellets turned green; extraction with water followed by acidification gave a dark blue precipitate, m.p. 250° C. (decomp.), identified as 1-(3′,4′-dihydroxy-1′-naphthyl)-3,4-naphthoquinone (m.p. 245° C. (sinters), 255° C. (decomp.) (18)).

A white crystalline compound was obtained from a 7% oxidized "alkali" run by extraction with water and acidification. Recrystallization from boiling water gave β-2-carboxyphenylpropionic acid (m.p. and mixed m.p. 164° C.).

DISCUSSION

The results given in Fig. 1 and Table I show that the initial catalysis by alkali is soon replaced by a strong inhibition. Although nearly all phenols act as inhibitors in the initial stages of the autoxidation of hydrocarbons, only certain easily oxidized ones such as the naphthols are also effective once the reaction has started (15). The oxidation of tetralin in the presence of strong alkali must therefore produce some powerful inhibitors.

It is clear from the experiments with the solid and liquid phases of a sodium hydroxide run that the inhibitor is only slightly soluble in tetralin, which suggests that the inhibitor is acidic and forms a salt with the alkali.

The very rapid conversion of tetralin hydroperoxide to 1-tetralone by hot alkali (11) was confirmed by infrared analysis. When alkali was added in the middle of a "normal" run the subsequent course of the reaction was of the "alkali" type, but the maximum rate (3.9) was only about one fifth of the rate reached when alkali was added at the start of a run (20.0). This indicates that inhibition depends on the reaction of alkali with 1-tetralone. An "alkali" run has to proceed to just over 1% oxidation before the rate starts to decrease, but when alkali is added in the middle of a "normal" run, the immediate conversion of tetralin hydroperoxide to 1-tetralone almost eliminates the catalytic effect of the alkali. The strong inhibition of the reaction by 1-tetralone and alkali (Table II) is therefore not unexpected; it is probably due in part to a base catalyzed enolization of 1-tetralone to 1-hydroxy-3,4-dihydronaphthalene on the surface of the alkali, and in part to the further oxidation products of 1-tetralone (see below).

The spectrum of colors through which the "alkali" reaction proceeds is very suggestive when compared with the results of Strauss, Bernouilly, and Mautner (18). These workers oxidized 2-hydroxy-1-tetralone in alkaline solution. The solution went through the color changes yellow, brown, greenish-brown, pure green, dirty green, and finally to a permanent orange. They identified the various colored compounds as 1,2-dihydroxynaphthalene (yellow); 3,4;3′,4′-tetrahydroxy-1,1′-dinaphthyl (brown in alkaline solution, pinkish-yellow in acid); 1-(3′,4′-dihydroxy-1′-naphthyl)-3,4-naphthoquinone (dark green in alkali, dark blue in acid); 2-hydroxy-1,4-naphthoquinone (orange in alkali, sodium salt red, yellow in acid). The last named compound was the end product of the reaction and did not further absorb oxygen under their experimental conditions. These substituted naphthols are all acidic and form insoluble salts; they are powerful oxidation inhibitors. While complete reliance can rarely be placed on color reactions alone, the identification in the present work of the last two compounds, and the fact that the "alkali" reaction goes through an almost identical color sequence, would seem to indicate that the first two products are probably also formed.

In agreement with the results of Robertson and Waters (16), no γ-2-hydroxyphenylbutyric acid was detected. These workers found that although this acid was produced by the autoxidation of tetralin and by the decomposition of tetralin hydroperoxide, it was not produced by the autoxidation of 1-tetralone. They concluded that it was formed by an ionic mechanism involving 1-tetra-

lone and tetralin hydroperoxide. In the "alkali" reaction there is of course little or no hydroperoxide present and therefore no γ-2-hydroxyphenylbutyric acid would be expected. Ring scission yields instead β-2-carboxyphenylpropionic acid. The formation of this acid instead of the phenolic acid can be compared with the action of acids and bases on the decomposition of cumene hydroperoxide (12). In the presence of acids this hydroperoxide breaks between the ring and the α carbon atom to yield phenol and acetone, but in the presence of alkali it is the bond between the α and β carbon atoms which breaks to give acetophenone and methane.

No 1-tetralol was detected in the alkaline oxidation of tetralin.

The effect of weak alkali on the oxidation of tetralin was intermediate between "normal" and "alkali" oxidations. This supports the belief that inhibition is due in part to a base catalyzed enolization of 1-tetralone. The amount of enolization, and hence the inhibition, depends both on the strength of the alkali and on its concentration, or more probably on its surface area.

The slight reduction in the rate of oxidation of tetralin by 1-tetralone is in agreement with earlier work (9, 13). Acetophenone behaves in the same way. The greater inhibition produced by partly oxidized 1-tetralone is due to the presence of the inhibitor 3,4-dihydro-1,2-naphthoquinone or its isomer 1-keto-2-hydroxy-1,4-dihydronaphthalene (16). The elimination of the normal induction period by the addition of *n*-valerophenone is similar to the technical use of ketones in promoting the autoxidation of hydrocarbons (19).

The results given in Table III indicate that inhibition by *n*-valerophenone and alkali is probably also due to a base catalyzed enolization on the surface of the alkali. The greater inhibition produced by a partially oxidized *n*-valerophenone and alkali mixture is similar to the increased inhibition produced by oxidized 1-tetralone.

The results in Table IV present some slight evidence that inhibition can also be produced by an acid catalyzed enolization of *n*-valerophenone, although the effect is much less marked than that produced by alkali. The effect shows up most clearly where the catalysis by *n*-valerophenone is compensated for, i.e. in a comparison of the times required to reach a given percentage oxidation for ketone plus potassium hydrogen phthalate and for ketone plus phthalic acid. The latter is a much slower reaction.

Alcohols have been reported both to decrease (15) and to increase (5) the rate of oxidation of tetralin. In the present work benzyl alcohol was found to act as a weak inhibitor.

The complete inhibition brought about by the addition of dehydrating agents at the start of the reaction is probably due to the dehydration of the hydroperoxide directly to 1-tetralone. This prevents chain branching which is normally brought about by scission of the O—O bond of the hydroperoxide.

The very sharp maximum in the "alkali" rate curve could be due to the build-up of sufficient inhibitor to reverse the initial catalyses. However two or more consecutive autocatalytic reactions can lead to periodicity in the reaction rate (14), and a close examination of the rate curves reveals that there are probably at least two subsidiary maxima. The whole course of the "alkali"

reaction might therefore also be explained as a consecutive series of autocatalytic reactions, the formation of inhibitors accounting for the decrease in height of successive maxima.

CONCLUSION

The usual method of reducing the rate of oxidative deterioration of hydrocarbons is by the addition of certain strong inhibitors such as aromatic amines and naphthols. These inhibitors are, however, gradually oxidized and therefore lose their effectiveness. Inhibition by alkali of the oxidation of tetralin, and presumably of many other hydrocarbons, offers certain advantages in that the concentration of inhibitors is maintained by the oxidation process. The most effective stabilization would probably be obtained by the use of both methods.

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MYRISTIC ACID MONOLAYER AT LOW SURFACE PRESSURES[1]

By G. P. Semeluk,[2] J. W. V. Hahn,[3] and John L. Morrison[4]

ABSTRACT

The surface pressure–area relationships of gaseous myristic acid films at the air–aqueous interface have been measured at very low surface pressures. The acid was spread from petroleum ether solutions. The molecular cohesion was found to be about six times that of gaseous butane under comparable conditions. Some explanation of Moss and Rideal's "double molecule" phenomenon is given.

A number of studies have already been made of myristic acid monolayers on water surfaces (2, 3, 4, 7, 8). Different types of apparatus have yielded concurring results (2, 3, 4) as well as anomalous ones (7, 8). Often insufficient data has been given concerning the methods of spreading, the concentration of the spreading solutions, and the time allowed for evaporation of the solvent, all of which are very important for monolayer studies at the low pressures of gaseous films. It is still correct to say that "Further work on gaseous films, with very sensitive instruments at areas over 1,000 sq. A., is desirable." (1, p. 43).

EXPERIMENTAL

Apparatus

A horizontal film balance of the Langmuir–Adam type (1) was used with an original modification which permitted a sweeping of the whole surface at one time (5). In this modification the head and mica float were vertically moved by a cam. Small stirrups held gold foil ribbons against the bakelized aluminum trough during film measurements. The other ends of the S-shaped ribbons were attached to the mica float to prevent leaks. On raising the head, the small stirrups raised the gold ribbons, and aluminum wire stirrups raised the float. Fragile parts of the head were specially clamped during these operations. The trough had a total area of 960 cm.^{2} and a film dispersing area of 687 cm.^{2}

The forces on the float were measured by phosphor bronze torsion wires. The 5 mil diameter wire measured forces from 0.01 to 1 dyne cm.$^{-1}$. The 3 mil wire measured forces from 0.010 to 0.1 dyne cm.$^{-1}$ to an accuracy of about 0.001 dyne.

Forces were registered by float movements which were transferred through a lever to a mirror pivoted on a torsion wire axle. The balance was used as a null instrument, readings being made on a calibrated dial.

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta. This paper is taken from theses submitted to the University of Alberta in partial fulfillment of the requirements for M.Sc. degrees.
[2]*Graduate student, 1948–48. Holder of a National Research Council Bursary. Present address: Electrochemical Laboratories Corporation, Tulsa, Oklahoma.*
[3]*Graduate student, 1944–46. Present address: Rheumatic Fever Research Institute, Chicago, Illinois.*
[4]*Associate Professor of Chemistry, University of Alberta, Edmonton, Alberta.*

Surface potential measurements were made with a polonium-coated air electrode and a calomel half cell. The potential was amplified by a Dubridge and Brown circuit using an FP 54 electron tube (10). The polonium electrode was mounted on a movable frame to explore the whole surface.

The surface balance was completely enclosed in a double wall copper box which was thermostatted at $20\pm0.1°$ C. A small door in a double wall plexiglass front face provided entry to the balance.

Materials

Myristic acid from Eastman Kodak Co. was recrystallized three times from absolute ethanol with norite treatment before each crystallization. The product melted sharply at 58° C.

The spreading solvents were petroleum ether (b.p. 30–35° C.) and benzene (thiophene-free). They were refluxed for 12 hr. over phosphorus pentoxide and then slowly fractionated in a combined reflux and fractionating column.

Solutions of myristic acid in each of the solvents were prepared and used immediately. Concentrations ranged from 0.0011 mgm. myristic acid per ml. to 0.0172 mgm. $ml.^{-1}$ in the case of petroleum ether which was the better solvent.

Procedure

The trough was filled to its brim with 0.01 *N* HCl in conductivity water. The solution had been previously treated with norite to remove surface active impurities. The surface was swept 10 times, the balance head lowered, and the zero point allowed to come to rest.

Each film was spread drop by drop over different parts of the surface from a 0.0878 ml. micropipette. A standard 10 min., determined from a preliminary study of spreading times, was allowed for solvent evaporation and spreading of the film.

Two types of experiments were made. For all areas below 7000 $Å^2$ $molecule^{-1}$, the 5 mil wire was used and the conventional procedure of successively decreasing the surface area was followed. The interval between successive force readings was from 6 to 10 min. For areas above 7000 $Å^2$, the 3 mil wire was used and a single determination of force and area was made. The surface was then swept clean and a new film was spread on a different area. Although the latter method was laborious, each reading taking about 45 min., it avoided any vibrations which cause zero point changes.

Surface potential measurements were determined only on the less dilute films. In very dilute films too few molecules were under the electrode (1 $cm.^2$ in area) to cause a potential change.

Complete details of the great precautions necessary to ensure cleanliness and stability are given elsewhere (9).

RESULTS AND DISCUSSION

The results for myristic acid dispersed from petroleum ether and from benzene are plotted in Fig. 1 as the surface pressure, F dyne $cm.^{-1}$, against the area, A, Angstrom^2 per molecule, following the notation of Adam (1). They are also plotted in Fig. 2 as the product FA against F. In this figure the results

of Adam and Jessop (2), Guastalla (4), and Allan and Alexander (3) are given for comparison with the present results. The present results, particularly for the single value experiments, are at lower pressures than any reported in the literature.

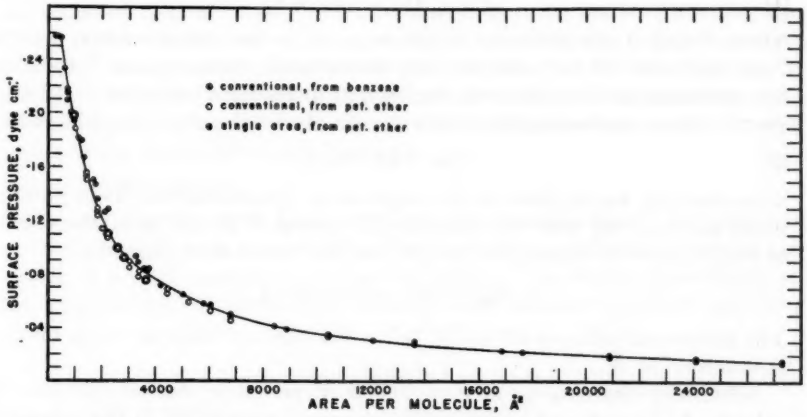

FIG. 1. Surface pressures corresponding to various surface areas occupied by myristic acid molecules on 0.01 *N* HCl aqueous solution.

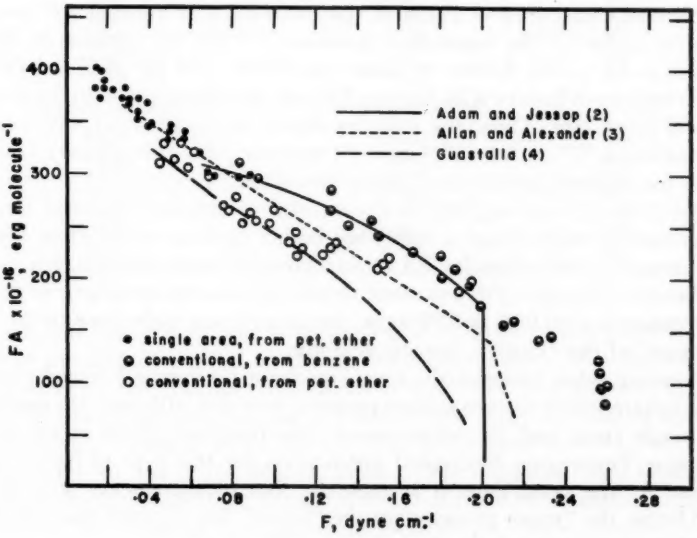

FIG. 2. Comparisons of *FA* versus *F* plots.

Although our results do not agree with those of Moss and Rideal (8), some experimental evidence will be given which may account for their observations. Also, an explanation will be suggested for the observations of Kalousek (7).

Cohesive Force

Corresponding to van der Waals equation for three dimensions, an equation for two-dimensional surface films (1, p. 120) would be

$$[1] \qquad (F+\alpha/A^2)(A-\beta) = kT$$

where F and A are the same as above, α/A^2 is the cohesive force, β is the "excluded area" of the molecules, k is Boltzmann's constant, and T the absolute temperature. In the present case, at very low surface pressures (<0.1 dyne cm.$^{-1}$), β becomes negligible compared with A and the equation reduces to

$$[2] \qquad FA = kT-\alpha/A.$$

This equation was applied to the single point determinations (29 in number) made on the 3 mil wire. By plotting FA against $1/A$ and using the method of least squares to obtain the straight line, we obtained the equation

$$FA = 402-4.02\times10^5/A.$$

The theoretical value of kT at 293° K. is 404 ergs per molecule when the area is expressed in Å^2.

Arbitrarily choosing an area of 12,000 Å^2 per molecule, we calculate the cohesive force α/A^2 to be 2.80×10^{-3} dyne cm.$^{-1}$ molecule^{-1}. If the film thickness is assumed to be 4.5 Å (1, p. 45), then α/A^2 is equivalent to 6.1×10^{-2} atm. cm.$^{-2}$ in three dimensions.

This cohesive force may be compared with that of butane under similar conditions. Thus, at A = 12,000 Å^2 per myristic acid molecule, F is equal to 0.03 dyne cm.$^{-1}$. The equivalent pressure in three dimensions at 20° C. is 0.66 atm. (1, p. 45). Under the same conditions, and for ideal behavior, the molar volume of butane is 36.4 liters. The van der Waals constant for butane, a, is 14.5 liter^2 atm. Thus, the cohesive forces are $a/V^2 = 1.1\times10^{-2}$ atm. for butane and $\alpha/V^2 = 6.1\times10^{-2}$ atm. for myristic acid. This is a very reasonable value for myristic acid in the gaseous film state.

Equation [2] was applied to the results of the conventional force–area experiments, which cover a somewhat higher pressure range than the single experiments. Low values for FA at zero pressure were obtained. For example, for benzene solutions FA was equal to 335. This is not surprising as the range of pressure is from 0.08 to 0.22 dyne, the latter being quite close to the "vapor pressure" of the "liquid" myristic acid film.

However, when extrapolations were made on FA versus F straight lines, the least square values at zero surface pressure were 410, 405, and 419 respectively for single runs, and for conventional runs from petroleum ether and from benzene. There is no theoretical justification for this type of *linear* extrapolation. At the same time, it is apparent that measurements must be made well below the "vapor pressure" of the "liquid" film in order that the van der Waals type of extrapolation be valid.

Latent Heat of Vaporization

Adam and Jessop (2), using the Clapeyron equation, have calculated the latent heat of vaporization of myristic acid liquid monolayer to be 3200 cal.

mole^{-1} at 14.5° C. The latent heat can also be estimated by combining their vapor pressure measurements at 14.5° (0.203 dyne) with ours at 20° (0.258 dyne from Fig. 2) in the Clausius–Clapeyron equation. By making the approximation that the latent heat is constant over this temperature range, we obtain the value of 730 cal. mole^{-1}. Two comments may be made concerning this value: (1) one would expect the latent heat to fall off rapidly with temperature near the "critical temperature" of the gaseous film (est. 30–35° (2)); (2) the present calculation takes more account of the effect of the substrate than does the method using the areas of the liquid and gaseous films at the terminal points of the liquid–gas equilibrium line.

The Island Phenomenon

For areas less than 6000 Å^2 per molecule, force readings taken at successively smaller areas, in each case 10 min. after spreading, exhibited an erratic behavior. A typical experiment is given in Table I. The surface potential apparatus showed that the film was not homogeneous. Wherever a drop of spreading

TABLE I

Area, Å^2 molecule^{-1}	Force, dyne cm.$^{-1}$	*FA*
Experiment No. 73 (0.0878 ml. of 0.0043 mgm. ml.$^{-1}$ in petroleum ether):		
6820	0.045	307
6020	0.097	583
5220	0.09	470
4410	0.09	395
3610	0.126	455
2810	0.12	335
2010	0.172	346
Repeat of Experiment No. 73 after decompression:		
6820	0.045	307
6020	0.052	313
5220	0.058	303
4410	0.068	300
3610	0.074	267
2810	0.091	256
2010	0.113	227

solution had been placed, the potential was 5 to 10 mv. more positive. Other parts of the surface showed no change from the potential of a clean surface. These observations suggest the presence of islands of unspread myristic acid. Since the islands did not disperse in a convenient length of time, a procedure was devised to disperse them. The film was compressed to one-seventh of its original area to merge the islands, then it was expanded very slowly (10–15 min.). Surface potentials varied over the surface to a smaller extent (2–6 mv.) and no clean surface potentials were found. After complete decompression, the compression was repeated with much more consistent results. It was found that the increased time did not accumulate much contamination.

The island phenomenon was observed for both benzene and petroleum ether solvents. It was also found to depend on the concentration of the dis-

persing solution. For example, when measurements were made at the lowest pressure range with the 3 mil torsion wire, solutions more dilute than 0.0043 mgm. per ml. spread completely in 10 min.

Further observations help to account for the island phenomenon. Immediately after placing the dispersing solution on the surface, the pressure increased momentarily to a fairly high value (approx. 0.3 dyne), then rapidly decreased practically to zero within a minute, and finally increased slowly for the next few minutes. Each drop of solution formed a lens of from 2 to 3 cm. diam. According to Harkins' theory of spreading (6), there is a monomolecular layer of hydrocarbon in equilibrium with a visible liquid lens. This would account for the high initial pressure. Apparently this monomolecular layer (5–10 Å thick) is not able to drag many myristic acid molecules with it. Most of them remain at the site of the lens, and the lens decreases largely by spreading as a monolayer and *then* evaporating.

The erratic force measurements can be explained[5] by the suggestion that each island of myristic acid will exert a dynamic vapor pressure in excess of the final static pressure of the homogeneous film. The mica float would pick up these dynamic pressures when islands floated near to it. Conversely, the absence of islands near the float would be similar to a two-dimensional vacuum. It is to be noted that this phenomenon is not the same as the incomplete spreading caused by contamination. In the latter case, the surface pressure is uniform over the whole surface.

Double Molecules

Moss and Rideal (8) determined the force–area relations of myristic acid films within the molecular area range of 1000 to 15,000 Å^2. They found a nearly constant value for FA of about 200 over the whole gaseous range. They concluded that the film consists of extremely stable double molecules, and that these follow the two-dimensional ideal gas law.

Moss and Rideal's spreading method differed from the one used here. Instead of obtaining successively smaller areas by moving a barrier towards the float, they used a fixed area. They spread a film from one drop of a solution, then they made a force measurement. Another drop was placed on top of the existing film to obtain a smaller molecular area and again a force measurement was taken. A series of such measurements on films spread one on top of the other comprised their experiment.

We duplicated the results of Moss and Rideal to a large extent by repeating their method of spreading on a fixed area. Initially 0.0878 ml. of a petroleum ether solution containing 0.0021 mgm. myristic acid per ml. solution was placed on a surface area of 662 sq. cm. After complete spreading of the film, duplicate amounts were placed successively on top of each film. The results are given in Fig. 3. In view of the fact that the first film spread on a clean surface did not give a FA value near 200 and the further fact that the island phenomenon disappeared as the initial areas became much greater than

[5]*The first referee has observed even* negative *pressures under conditions similar to the above and suggests that the observations may be accounted for by a cooling caused by the evaporating volatile solvent.*

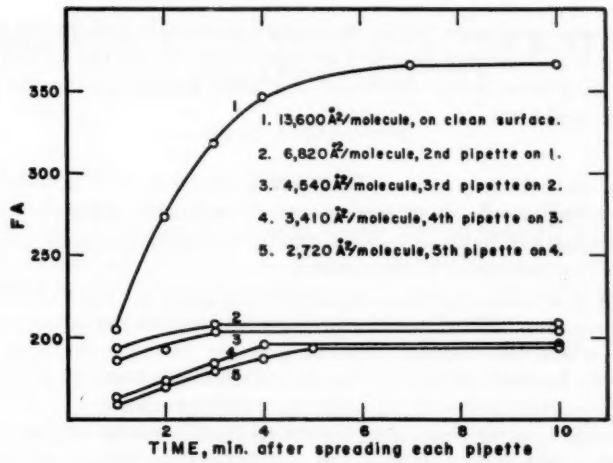

FIG. 3. The changes of surface pressure with time after adding one spreading solution on top of another at constant surface area.

7000 Å² per molecule, it is possible that a critical concentration of the spreading solution exists above which there is spontaneous double molecule formation.[6,7]

As the island phenomenon was most pronounced with solutions of concentration 0.0043 mgm. ml.$^{-1}$ and greater, it is believed that this is near the critical concentration. Unfortunately, Moss and Rideal, in common with most workers in this field, did not report their spreading solution concentrations. Moreover their experimental temperature (17°) would be more favorable to double molecule formation than ours.

The time of spreading is very important. In our case, the one minute reading for each pipette (Fig. 3) is obtained *after* the rise caused by the petroleum ether has fallen off. Adam (1, p. 31) suggests taking readings within one minute. Moss and Rideal allowed "a few minutes" between readings. It is apparent from our results that even for such a volatile solvent as petroleum ether (b.p. 30–35°) at least six minutes are required to obtain a steady force reading.

It may be possible to explain Kalousek's anomalous results for myristic acid (7). His results for the ester ethyl hexadecanedicarboxylate are normal, extrapolating to an *FA* value of about 400. However, his myristic acid *FA* values only reach about 65 at 0.014 dyne cm.$^{-1}$. Although he gives no data on the concentrations of his spreading solutions, a clue to their magnitude may be given in his statement—"This condition is fulfilled with light petroleum (b.p. 70°) which in amounts of 1 mm.^{3}/100 cm.^{2} evaporates in about 1 minute." If he used this volume for his spreading solutions, then his concentrations would be of the order of 10 times the present ones. Such high concentrations

[6] *The significance of the concentration of the spreading solution was not fully realized at the time these measurements were made so that other initial spreading concentrations were not tested.*

[7] *The first referee has suggested that Moss and Rideal* may *have used water as a substrate* and *an uncoated metal trough for their balance. Either or both these differences in method may account for their anomalous results.*

would be very conducive to the occurrence of islands and double molecules. In his efforts to overcome the effect of residual solvent on the surface pressure, Kalousek may have become involved in a more serious error in the spreading of myristic acid films.

Solvents

Each of the solvents, benzene and petroleum ether, has its disadvantages. Our low boiling petroleum ether evaporated too quickly, which was conducive to island formation. Benzene leaves a significant residual pressure and increases the rate of contamination of the surface.

Because of residual pressure, measurements made on benzene solutions at areas greater than 2750 Å^2 were not reliable. At surface pressures greater than 0.2 dyne, where the residual pressure was less than one-tenth of the total pressure, the benzene and petroleum ether results coincided. The surface vapor pressure of myristic acid was the same from both solvents.

The change in surface potential for the residual benzene, compared with the clean surface, was about −3 mv. at 10 min. Myristic acid changes the potential in the opposite direction. Petroleum ether evaporated completely in 10 min. to leave the surface potential unchanged. Thus, the latter is the more suitable solvent for surface potential measurements.

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APPLICATION OF THE VIBRATIONAL SUM RULE TO HALOGENATED ETHYLENES[1]

By H. J. Bernstein

ABSTRACT

The vibrational sum rule has been applied to the fluoro-chloro-bromo-ethylenes and good agreement obtained between observed frequency sums and those calculated on the basis of additivity considerations. Two unobserved frequencies for *trans* dibromoethylene have been calculated and the in-plane and out-of-plane sums for some molecules not yet investigated. Several ambiguities with regard to some halogenated ethylenes have been resolved and several assignments which merit reinvestigation have been indicated.

Considering the zero-point energy in a homologous series of molecules to be an additive property, analogous to the heat of atomization for example, indicated that the sum of the frequencies of the fundamental modes of vibration could be treated as an additive property (2). The additivity scheme describing these properties was one in which contributions from bonds, interactions between neighboring bonds and/or atoms, and interactions between next neighboring bonds, etc., were taken into account (1).

New vibrational data for several halogenated ethylenes have been reported recently and it seems worth while at this time to show the kind of agreement that can be obtained between observed frequency sums and those calculated on the basis of the additivity model. On the strength of this agreement it is then possible to predict some frequency sums for molecules which as yet have not been investigated spectroscopically and also disclose existing assignments which merit reinvestigation.

The relations derived (1) for the substituted ethylenes $C_2X_{4-n}Y_n$ are given in Table I. In making use of the sum rule* it is often required to estimate two

TABLE I

Σ_*

n		P	a	b	c	d
0	C_2X_4	1				
1	C_2X_3Y	1	1			
2	*cis* $C_2X_2Y_2$	1	1			1
2	*trans* $C_2X_2Y_2$	1	1		1	
2	*asym* $C_2X_2Y_2$	1	1	1		
3	C_2XY_3	1	0	1	1	1
4	C_2Y_4	1	−2	2	2	2

unobserved missing sums when the parameters of Table I have been evaluated from the five minimum data. To illustrate the agreement obtained under these

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**The sums formed from the observed fundamental frequencies include gas and/or liquid and/or dilute solution values for the frequencies since vapor state data are not always available.*

conditions, five of the six observed sums for the bromoethylenes have been used to evaluate four sets of values for the parameters of Table I and then used to calculate the unobserved frequency sum for the *trans* molecule and the sixth observed sum. The results are shown in Table II in which the dashes

TABLE II

$\Sigma\nu$

	Observed	Calculated			
C_2H_4	21597[a]	21648	—	—	—
C_2H_3Br	17795[b]	—	17770	—	—
cis $C_2H_2Br_2$	13920[c]	—	—	—	—
trans $C_2H_2Br_2$	—	13727	13710	13813	13788
asym $C_2H_2Br_2$	13810[d]	—	—	—	—
C_2HBr_3	9730[c]	—	—	9755	—
C_2Br_4	5518[e]	—	—	—	5467

[a]*Arnett, R. H. and Crawford, B. L. J. Chem. Phys. 18: 118. 1950; with the new value of* $\nu_b(b_{1g})$ *found by B. P. Stoicheff, J. Chem. Phys. 21: 755. 1953.*
[b]*Charette, J. and de Hemptinne, M. Bull. classe sci., Acad. roy. Belg. 38: 934. 1952.*
[c]*Reference (5).*
[d]*de Hemptinne, M. Trans. Faraday Soc. 42: 7. 1946.*
[e]*Reference (7).*

represent frequency sums used to evaluate the parameters. Comparison of the observed and calculated value for the sixth sum indicates agreement to within ± 50 cm.$^{-1}$. The average of the calculated values of the unobserved *trans* sum has an average deviation from the mean of 41 cm.$^{-1}$.

Since the potential energy function for the nine in-plane and three out-of-plane vibrations of a substituted ethylene may be separated, one might expect that the relations of Table I are valid both for the in-plane and for the out-of-plane frequency sums as well as for the total sums. This has already been verified for the chloroethylenes (2).

In Tables III and IV the calculated frequency sums for the in-plane and out-of-plane modes for the bromoethylenes are given, corresponding to the calculations shown in Table II for the total sums.

TABLE III

IN-PLANE SUMS FOR BROMOETHYLENES

	Observed	Calculated			
C_2H_4	18678[a]	18682	—	—	—
C_2H_3Br	15364[b]	—	15362	—	—
cis $C_2H_2Br_2$	12020[c]	—	—	—	—
trans $C_2H_2Br_2$		11943	11951	11959	11957
asym $C_2H_2Br_2$	11831[d]	—	—	—	—
C_2HBr_3	8394[c]	—	—	8396	—
C_2Br_4	4742[e]	—	—	—	4736

All footnotes are the same as for Table II.

TABLE IV

OUT-OF-PLANE SUMS FOR THE BROMOETHYLENES

	Observed	Calculated			
C_2H_4	2919[a]	2966	—	—	—
C_2H_3Br	2431[b]	—	2408	—	—
cis $C_2H_2Br_2$	1900[c]	—	—	—	—
trans $C_2H_2Br_2$		1785	1762	1854	1831
asym $C_2H_2Br_2$	1979[d]	—	—	—	—
C_2HBr_3	1336[e]	—	—	1359	—
C_2Br_4	775[e]	—	—	—	729

All footnotes are the same as for Table II.

From Table III it is seen that the calculated sum for *trans* $C_2H_2Br_2$ is very nearly the same for all solutions and that the agreement for the sixth sum is quite good. Since all but one of the in-plane fundamentals are known (3) for *trans* $C_2H_2Br_2$ the unobserved fundamental may be estimated from the sum in Table III to be 149 ± 6 cm.$^{-1}$. Similarly the unobserved out-of-plane mode (3) for *trans* $C_2H_2Br_2$ may be estimated at 170 ± 50 cm.$^{-1}$. Applying the above method to the recent data (7) for the fluorochloroethylenes gives the results shown in Tables V and VI.

TABLE V

IN-PLANE SUMS FOR THE FLUOROCHLOROETHYLENES

	Observed[a]	Calculated			
C_2F_4	8234	8193	—	—	—
C_2F_3Cl	7591	—	7612	—	—
cis $C_2F_2Cl_2$		6985	7004	6904	6944
trans $C_2F_2Cl_2$	6909	—	—	—	—
asym $C_2F_2Cl_2$	7066	—	—	—	—
C_2FCl_3	6380	—	—	6360	—
C_2Cl_4	5771	—	—	—	5812

[a] *The data are from Reference (7).*

TABLE VI

OUT-OF-PLANE SUMS FOR THE FLUOROCHLOROETHYLENES

	Observed[a]	Calculated			
C_2F_4	1104	1102	—	—	—
C_2F_3Cl	1073	—	1071	—	—
cis $C_2F_2Cl_2$		1054	1055	1051	1052
trans $C_2F_2Cl_2$	998[b]	—	—	—	—
asym $C_2F_2Cl_2$	1044	—	—	—	—
C_2FCl_3	979	—	—	978	—
C_2Cl_4	914	—	—	—	916

[a] *The data are from Reference (7).*

[b] *This sum includes one frequency calculated by means of a normal coordinate treatment which gives over-all agreement between observed and calculated frequency of 1 to 2% for all the members of the series* $C_2F_4 \rightarrow C_2Cl_4$ *(Reference (7)).*

It is evident from Table I that the average of the frequency sums for *cis*, *trans*, and *asym* disubstituted ethylenes lies on a parabola passing through the sums for the other molecules when the frequency sum is plotted against the number of substituents n. Thus the X, Y, Z substituted ethylenes may be treated as the X, X, Z substituted methanes and the relations between their sums expressed in terms of the six parameters of Table III in Reference (1) and shown again for convenience in Tables VII and VIII. In Table VII the sums calculated with the least squares values of the parameters are compared with the observed sums for the chloro- and fluoro-ethylenes. In all cases the value for the disubstituted molecule is asterisked and is the average of the sums for the isomeric disubstituted molecules. The agreement between observed and calculated sums is rather good, being within ±25 cm.$^{-1}$ for the in-plane modes and ±10 cm.$^{-1}$ for the out-of-plane. The asterisked sum is only roughly

TABLE VII

	Parametric relations						$\sum\nu_{\text{in-plane modes}}$			$\sum\nu_{\text{out-of-plane modes}}$		
Molecule	P	α	β	γ	Δ_1	Δ_2	Calc.†	Obs.	Obs. − calc.	Calc.‡	Obs.	Obs. − calc.
C_2H_4	1						18697	18678[a]	−19	2919	2919[a]	0
C_2H_3Cl	1	1					15623	15659[b]	34	2453	2459[b]	+ 6
$C_2H_2Cl_2$*	1	2			−1		12442	12431[b]	−11	1962	1959[b]	− 3
C_2HCl_3	1	3			−3		9156	9133[b]	−23	1449	1447[b]	− 2
C_2Cl_4	1	4			−6		5763	5771[c]	8	913	914[c]	+ 1
C_2H_3F	1		1				16246	16251[d]	5	2514		
C_2HF_3	1		3			−3	11010	11004[e]	−6	1607	1610[e]	+ 3
C_2F_4	1		4			−6	8226	8234[c]	18	1105	1104[c]	− 1
C_2Cl_2F	1		1	3	−3		6370	6380[c]	10	977	979[c]	+ 2
C_2ClF_3	1	−2	3	3		−3	7601	7591[c,f]	−10	1074	1072[c,f]	− 2
$C_2Cl_2F_2$*	1	−2	2	4	−1	−1	6982	7004[c]	+22	1031	1020[c]	−11
$C_2H_2F_2$*	1		2			−1	13683	13463[g]		2076	2127[h]	
											2004[i]	
C_2H_2FCl*	1		1	1			13060			2025		
C_2Cl_2HF*	1		1	2	−1		9768			1513		
C_2F_2HCl*	1	−1	2	2		−1	10386	10422[j]		1565	1568[j]	

*For these molecules the sum is $\frac{1}{2}(\sum\nu_{cis}+\sum\nu_{trans}+\sum\nu_{asym})$.

†*The least squares values for the parameters used to obtain these calculated sums are* $P = 18697$, $\alpha = -3074.2$, $\beta = -2451.2$, $\gamma = -3185.8$, $\Delta_1 = 106.1$, *and* $\Delta_2 = 111.0$, *all in cm.*$^{-1}$.

‡*The least squares values for the parameters used to obtain these calculated sums are* $P = 2919$, $\alpha = -467$, $\beta = -406$, $\gamma = -489$, $\Delta_1 = 23.2$, *and* $\Delta_2 = 31.9$, *all in cm.*$^{-1}$.

[a]*Same as for Table II.*

[b]*Reference (2), except data for* C_2HCl_3 *are taken from Allen, G. and Bernstein, H. J. Can. J. Chem. 32: 1044. 1954.*

[c]*Reference (7).*

[d]*Torkington, P. and Thompson, H. W. Trans. Faraday Soc. 41: 236. 1945.*

[e]*Mann, D. E., Acquista, N., and Plyler, E. K. J. Chem. Phys. 22: 1586. 1954.*

[f]*Mann, D. E. Am. Chem. Soc. Meeting, New York, Sept. 1954. Also Smith, Nielsen, Berryman, Classen, and Hudson, N.R.L. Report 3567. Washington, D.C. Sept. 1949. p. 57.*

[g]*Sum for* $CH_2{=}CF_2$ *only. Smith, D. C., Nielsen, J. R., and Classen, H. H. J. Chem. Phys. 18: 326. 1950; Edgell, W. F. and Byrd, W. E. J. Chem. Phys. 17: 740. 1949; Torkington, P. and Thompson, H. W. Trans. Faraday Soc. 41: 236. 1945; and Edgell, W. F. and Altel, C. J. J. Chem. Phys. 22: 1983. 1954.*

[h]*Sum for* $CH_2{=}CF_2$ *only from Edgell et al. (Ref. g) and Torkington and Thompson (Ref. g).*

[i]*Sum for* $CH_2{=}CF_2$ *only from Smith et al. (Ref. g).*

[j]*Data for* $CF_2{=}CHCl$ *only from Nielsen, J. R., Liang, C. Y., and Smith, D. C. J. Chem. Phys. 20: 1090. 1952. These are included to indicate that the assignment of the above authors is consistent with the sum rule.*

TABLE VIII

Molecule	Parametric relations						$\sum\nu_{\text{in-plane modes}}$		$\sum\nu_{\text{out-of-plane modes}}$		
	P	α	β	γ	Δ_1	Δ_2	Calc.†	Obs.	Calc.‡	Obs.	
C_2H_4	1						18697	18678[a]	2919	2919[a]	
C_2H_3Br	1	1					15365	15362[b]	2440	2431[b]	
C_2HBr_3	1	3			−3		8387	8394[c]	1320	1336[c]	
C_2H_3F	1		1				16246	16251[d]	2514		
C_2HF_3	1		3			−3	11010	11004[e]	1607	1610[e]	
C_2F_4	1		4			−6	8226	8234[f]	1105	1104[f]	
C_2BrF_3	1	−2	3	3		−3	7354	7353[g]	1043	1043[g]	
$C_2H_2Br_2$*	1	2			−1		11929	11925[h]	1907	1935[h]	
C_2Br_4	1	4			−6		4743	4742[f]	679	674[f]	
$C_2H_2F_2$*	1		2			−1	13683	13463[i]	2076	2127[j]	2004[k]
C_2Br_3F	1		1	3	−3		5613		830		
$C_2Br_2F_2$*	1	−2	2	4	−1	−1	6484		951		
C_2H_2FBr*	1		1	1			12806		2006		
C_2Br_2HF*	1		1	2	−1		9261		1445		
C_2F_2HBr*	1	−1	2	2		−1	10136		1540		

*For these molecules the frequency sum is $\frac{1}{2}[\sum\nu_{cis}+\sum\nu_{trans}+\sum\nu_{asym}]$.

†Values of P, β, and Δ_2 are the same as for Table VII (footnote †), and $\alpha = -3332$, $\Delta_1 = 104.5$ were evaluated from the observed sums for C_2H_3Br, C_2HBr_3, and C_2Br_4 averaging the solutions for the three pairs of equations. $\gamma = -3440$ was then found from the observed sum for C_2BrF_3.

‡Values of P, β, and Δ_2 are the same as for Table VII (footnote ‡), and $\alpha = -479$, $\Delta_1 = 54$ were evaluated from the observed sums for C_2H_3Br, C_2HBr_3, and C_2Br_4 by averaging the solutions for the three pairs of equations. $\gamma = -507$ was then found from the observed sum for C_2BrF_3.

[a,b,c,d,e]Same as for Table II.

[f]Reference (7).

[g]Mann, D. E., Acquista, N., and Plyler, E. K. *J. Chem. Phys. 22: 1199. 1954.*

[h]Average of the cis and asym only from Reference (3) and M. de Hemptinne, *Trans. Faraday Soc. 42: 7. 1946*, respectively.

[i]Same as *g* of Table VII.

[j]Same as *h* of Table VII.

[k]Same as *i* of Table VII.

equal to the sum for each isomer so that observed sums for $CF_2{=}CHCl$ are given for comparison to indicate only that no gross error in assignment has been made. This is the case also for $C_2H_2Br_2$ and $C_2H_2F_2$ given in Table VIII. In Table VIII the least squares values of the parameters were not obtained since there is only one equation for evaluating γ. However, the same values of P, β, and Δ_2 were used as for the molecules in Table VII and α and Δ_1 obtained from the observed sums for C_2HBr_3, C_2H_3Br, and C_2Br_4 by averaging the solutions from the three pairs of equations thus provided. The value for γ was then obtained from the observed sums for C_2F_3Br. The estimated error in the calculated sums for the bromofluoroethylenes is about ± 50 cm.$^{-1}$ for the in-plane sums and about ± 25 cm.$^{-1}$ for the out-of-plane sums.

Several ambiguities with regard to the assignments of some halogenated ethylenes can be resolved by comparison of the observed and calculated sums. Also several assignments which require reinvestigation are indicated. In C_2H_3Br the assignment (Ref. *b* in Table VII) for the out-of-plane modes is consistent with the sum rule whereas that given by Kohlrausch (4) and that given in Ref. *d* of Table VII are not. In C_2H_3F the assignment given in Ref. *d* of Table VII for the out-of-plane modes is not consistent with the sum rule. For C_2F_3Cl the assignment of Mann *et al.* (5) for the in-plane modes is con-

sistent with the sum rule. For C_2F_3Cl the assignment of Mann *et al.* (5) for the in-plane modes is consistent with the sum rule but that of Smith *et al.* (Ref. *f* of Table VII) is not. For C_2FCl_3 the assignments of Mann and Plyler (6) and Nielsen *et al.* (Ref. *f* of Table VII) for the in-plane modes are not consistent with the sum rule. All recent assignments for the fluorochloroethylenes of Mann and Plyler (7) are consistent with the sum rule.

As shown in Ref. (2) the theory predicts the following relationship between the frequency sum of the molecules and their deuterated analogues:

$$\sum\nu_{C_2H_{4-n}X_n} - \sum\nu_{C_2D_{4-n}X_n} = (1-n/4)\left\{\sum\nu_{C_2H_4} - \sum\nu_{C_2D_4}\right\}.$$

This equation is valid also for each of the isomeric disubstituted ethylenes. Using this equation for the in-plane and out-of-plane sums, the sums shown in Table IX have been calculated for some deuterated fluoro- and bromo-

TABLE IX

	$\sum\nu_{\text{in-plane}}$		$\sum\nu_{\text{out-of-plane}}$	
	Calc.	Obs.	Calc.	Obs.
C_2D_3Br	12044		1912	
cis $C_2D_2Br_2$	9814	9767[a]	1554	1545[a]
1.1 $C_2D_2Br_2$	9625		1663	
C_2DBr_3	7291		1163	
C_2D_3F	12933		2003	
1.1 $C_2D_2F_2$	11257	11259[b]	1730	1755[b]
C_2DF_3	9901	9803[c]	1437	1431[c]

[a] *Professor M. de Hemptinne, private communication, Oct. 21, 1954.*
[b] *From the data of Edgell and Altel (Ref. g of Table VII).*
[c] *Ref. e, Table VII.*

ethylenes. The sums for C_2D_4 are given in Ref. *a* of Table II. The corresponding calculations for the frequency sum of the deuterated chloroethylenes have been given elsewhere (2).

Graphical Methods

If the frequency sums for two homologous series of substituted ethylenes are quadratic functions of the number of substituents, then there is a quadratic relationship between the frequency sums for the molecules of one series and those of the corresponding molecules of the other series (3). It has been discussed previously (3) under what conditions this relationship between the two sets of frequency sums becomes nearly linear, namely, if the ranges of frequency sums for both series are large and of the same order of magnitude and/or the deviation from linearity of the frequency sum as a function of the number of substituents is small. These conditions are fulfilled approximately for the chloro-, fluoro-, and bromo-ethylenes and the linear plots for the in-plane sums are shown in Fig. 1. To form the average of the sums of the isomeric disubstituted molecules the calculated sum for the molecule whose spectrum is unknown has been used (see Tables II to VIII). In Fig. 2 the corresponding

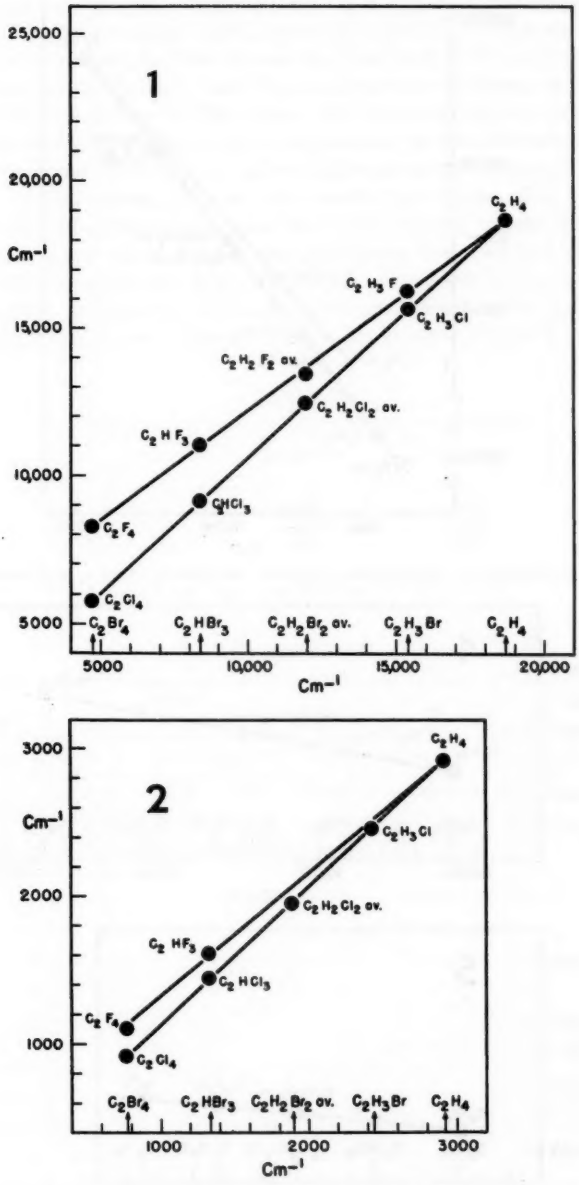

FIG. 1. The in-plane sums for the fluoro- and chloro-ethylenes plotted against the in-plane sums for corresponding bromoethylenes.

FIG. 2. The out-of-plane sums for the fluoro- and chloro-ethylenes plotted against the out-of-plane sums for the corresponding bromoethylenes.

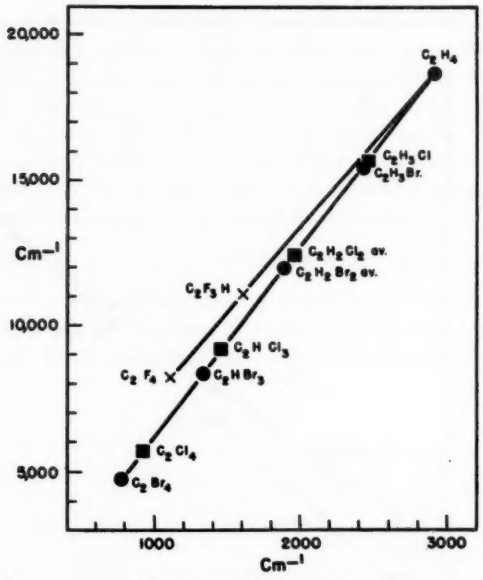

FIG. 3. The in-plane vs. out-of-plane sums for the fluoro-, chloro-, and bromo-ethylenes.

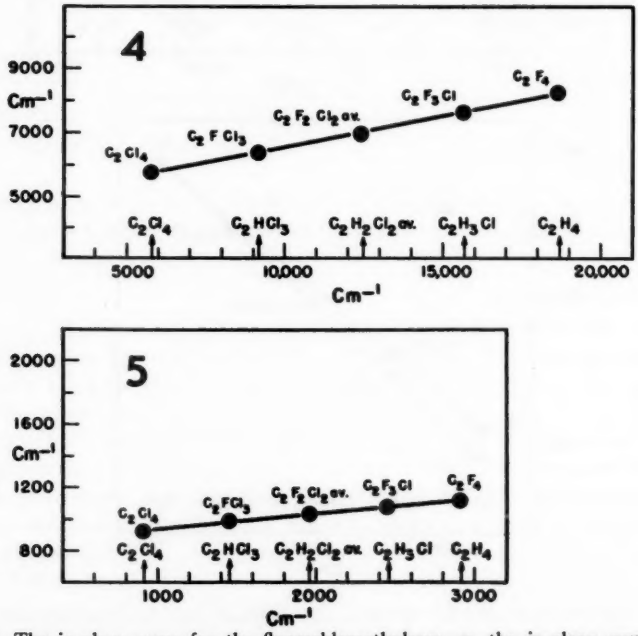

FIG. 4. The in-plane sums for the fluorochloroethylenes vs. the in-plane sums for the chloroethylenes.

FIG. 5. The out-of-plane sums for the fluorochloroethylenes vs. the out-of-plane sums for the chloroethylenes.

plots are given for the out-of-plane sums. It is apparent that a good internal check in the assignments for such a series is to plot the frequency sum for the in-plane modes against that for the out-of-plane modes. The resulting straight lines for the chloro-, bromo-, and fluoro-ethylenes are shown in Fig. 3. It is fortuitous that the points for the chloro- and bromo-ethylenes lie on the same straight line in Fig. 3. In Fig. 4 the in-plane sums for the fluorochloroethylenes are plotted against those for the chloroethylenes on the same scale and Fig. 5 shows the corresponding plot for the out-of-plane sums. The chlorofluoroethylenes and chlorobromoethylenes also fulfill approximately the conditions for obtaining linear plots so that the frequency sums for the chlorobromoethylenes may be estimated from the straight line given by the end members of the two series and reading off these sums from the values for the corresponding chlorofluoroethylenes. These estimates are given in Table X.

TABLE X

	$\sum \nu_{\text{in-plane}}$	$\sum \nu_{\text{out-of-plane}}$
C_2ClBr_3	5015	713
$C_2Cl_2Br_2$	5260*	780*
C_2Cl_3Br	5520	830

**Asterisk has same significance as for Table VII.*

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A SYSTEM OF MOLECULAR THERMOCHEMISTRY FOR ORGANIC GASES AND LIQUIDS[1]

By Keith J. Laidler

ABSTRACT

An analysis has been made of the heats of formation and combustion of organic gases and liquids, and of the heats of vaporization of liquids. The work has been done as far as possible with homologous series, in order to discover systematic effects. The data are converted into heats of atomization, i.e., the heats required to convert the gases or liquids into their constituent atoms. It is shown that the heats of atomization of the gaseous aliphatic hydrocarbons (paraffins, olefins, and acetylenes) can be accurately represented by a scheme in which a distinction is made between primary, secondary, and tertiary carbon–hydrogen bonds, and between bonds that are next to, and next but one to, multiple bonds. For aromatic molecules an appropriate correction for resonance is proposed. For other types of compound it is found that suitable values for the various bonds (e.g., C–CHO, C–OH) will give rise to good agreement with experiment.

It is shown that to a reliable approximation heats of vaporization are also amenable to the same treatment. Since this is so it is possible to assign bond values on the basis of which it is possible to make predictions about heats of formation of liquids.

A system of coefficients is worked out by means of which the numbers of atoms of various kinds in a molecule can be expressed in terms of the numbers of the different kinds of bonds. On the basis of these it is shown how bond contributions to heats of formation and heats of combustion can be calculated. A table (Table X) gives the contributions proposed for the heats of atomization, heats of formation, and heats of combustion for both gases and liquids.

INTRODUCTION

Various attempts have been made from time to time to devise systems that will enable reliable values of heats of formation and of heats of combustion to be deduced on the basis of chemical structure. Very approximate values can be calculated assuming strict bond additivity, using bond strengths such as those listed by Pauling (26) and by Syrkin (37); however such a procedure can lead to considerable errors in organic molecules of even only moderate complexity. Various schemes for the inclusion of terms for interactions (27) between bonds or between atoms have been proposed, notably those of Taylor, Pignocco, and Rossini (42), Tatevskii (38, 39, 40), and Bernstein (4). Of these workers Taylor, Pignocco, and Rossini did not specifically consider heats of formation, but Tatevskii showed that reliable predictions could be made for paraffins by recognizing three different types of carbon–hydrogen bonds and 10 different types of carbon–carbon bonds. Bernstein later showed that equally good agreement could be obtained with fewer types. In the present paper it is shown that satisfactory agreement for the lower paraffins is obtained by treating all carbon–carbon bonds as the same and recognizing three different types of carbon–hydrogen bonds. For olefins and acetylenes six additional types of bonds are required, and in most cases it is shown that the scheme is equivalent to, but much simpler than, a scheme of near-neighbor interactions.

The present paper is restricted to organic compounds containing carbon, hydrogen, oxygen, and nitrogen only, but the methods are readily extended to

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Contribution from the Department of Chemistry, the University of Ottawa, Ottawa, Canada.

other substances. Bond contributions are arrived at that will allow heats of atomization, formation, and combustion of gaseous and liquid substances to be estimated in a reasonably reliable manner. The procedures employed are necessarily empirical ones, but as far as possible an attempt has been made to provide some theoretical basis for the method; this has been done by taking the heats of atomization as the fundamental quantities to be analyzed. The method differs in this respect from certain others, such as the very useful one of Andersen, Beyes, and Watson (3, 19) in which the conventional heats of formation are the basic quantities employed.

Heats of Formation, Atomization, and Combustion

Thermochemical data are generally quoted in terms of heats of formation, Q_f, which are the heats liberated when one mole of the substance is produced from the elements in their standard states, viz., gaseous hydrogen, oxygen, and nitrogen, and carbon in the form of graphite. The data at 25°C. are considerably more extensive than those at any other temperature (including 0°K.), and in the present paper data at this temperature will always be used.

For the present purposes the most convenient procedure, and certainly the most fundamental, is to make use of heats of atomization, Q_a, instead of the heats of formation. By the heat of atomization (which will again always be referred to 25°C.) is meant the work required to dissociate one mole of the substance into its constituent atoms in their ground states. In the present paper heats of atomization have been calculated from heats of formation by making use of the following thermochemical relationships, which apply at 25°C.:

$$C_{graphite} = C_{gaseous}(^3P) - 171.7 \text{ kcal.},$$
$$\tfrac{1}{2}H_2 = H - 52.09 \text{ kcal.},$$
$$\tfrac{1}{2}O_2 = O - 59.16 \text{ kcal.},$$
$$\tfrac{1}{2}N_2 = N - 113.0 \text{ kcal.}$$

Of these values all except the last are taken from the National Bureau of Standards tables (46), which are the source of most of the thermochemical data employed here. The second and third values are well established on the basis of spectroscopic and other results, but the first and last have been the subject of considerable controversy and can still not be said to have been firmly established. On the whole, in the author's opinion, the evidence seems to point fairly strongly to the values quoted. The value given for graphite is consistent with the direct determination of the heat of sublimation of graphite by Brewer, Gilles, and Jenkins (8), and with some more recent work (10, 18). Springall (33) (see also Laidler and Casey (23)) has reviewed the evidence and favors this value. The nitrogen value given above was first proposed by Gaydon (14), and has been supported by much later work (13, 17, 21, 43).

On the basis of the above relationships it is easily seen that heats of atomization are related to heats of formation by the formula

$$[1] \qquad Q_a = Q_f + 171.7n_C + 52.09n_H + 59.16n_O + 113.0n_N$$

where n_C, n_H, n_O, and n_N are the numbers of carbon, hydrogen, oxygen, and

nitrogen atoms in the molecule. Heats of formation are frequently calculated from heats of combustion, Q_c, the two being related (for a compound containing only C, H, O, and N) by

[2] $$Q_f = -Q_c + 94.05n_C + 34.16n_H.$$

This formula assumes the combustion to give rise to carbon dioxide and nitrogen, and water in the liquid state. It is consistent with the thermochemical values given in the N. B. S. tables, namely

$$Q_c(\text{graphite}) = 94.05, \qquad Q_c(H_2\ \text{gas}) = 68.32.$$

The above two relationships give rise to

[3] $$Q_a = -Q_c + 265.75n_C + 86.25n_H + 59.16n_O + 113.0n_N.$$

The Bond Strength

The bond strength is a measure of the strength of the bond as it exists in the molecule, and its value is assigned in a purely empirical manner so that the sum of the various bond strengths in a molecule is equal to the heat of atomization. The present paper is concerned with the problem of assigning bond strengths in a self-consistent manner.

With diatomic molecules the bond strength is equal to the dissociation energy. In a polyatomic molecule containing only one type of bond, such as methane, there is again no difficulty; the bond strength is simply the heat of atomization divided by the number of bonds. For molecules containing more than one type of bond, on the other hand, the bond strengths cannot be defined with such precision. The procedure in such cases is to devise a scheme of classifying bonds that will give rise to a self-consistent scheme for all the molecules for which there are adequate data; a value is assigned to each type of bond in such a manner that the sum of the bond strengths is equal to the heat of atomization in every case. In the simplest schemes, such as those of Pauling (26) and Syrkin (37), all bonds connecting the same pair of atoms are considered to be the same. By taking into account all sorts of interactions it is apparent that very complicated schemes can be developed. From the most practical point of view it is evident that the most useful scheme is one that combines simplicity with accuracy. The system proposed in the present paper is a very simple one in that a differentiation between bonds connecting the same pair of atoms is only made in the case of carbon–hydrogen bonds, which are classified into different types which are readily recognized. In the present state of thermochemical data (which as far as homologous series are concerned are very incomplete except for the hydrocarbons) it is doubtful whether a more elaborate scheme would be justified or would give more satisfactory agreement with the data. As additional data accumulate, however, it will doubtless be advantageous to differentiate between bonds connecting other pairs of atoms; a scheme for doing this is in fact outlined below.

HEATS OF ATOMIZATION OF GASES

The N. B. S. tables (46) include values for heats of formation of a considerable number of paraffins, olefins, acetylenes, and aromatic compounds.

With other classes of compounds, however, such as alcohols and nitrates, data for only a few scattered compounds are generally available. A more complete analysis can obviously be made for the former groups of compounds, and the bond strengths derived from these will be the backbone of the present system. The homologous series will be considered first, after which some values will be derived for bonds such as C–OH and C–ONO_2. The latter values will be subject to revision as more reliable and complete data become available.

The Paraffins

The inadequacy of the simple additive scheme for the paraffins, with all C–H bonds considered as the same, is readily demonstrated. Thus the bond strength in CH_4 is 398.0/4 = 99.5 kcal., and the assumption that this remains the same in ethane gives a C–C strength of 79.1 kcal. These values lead to a heat of atomization for *n*-hexane of 1788.5 kcal., whereas the observed value is 1799.5 kcal. The errors become greater as the size of the molecule increases.

The simplest way to effect some improvement is to classify carbon–hydrogen bonds as primary, secondary, and tertiary bonds. A primary bond is one that involves a carbon atom in common with two other C–H bonds (i.e. that appears in the structure $-CH_3$); a secondary bond is one that has a carbon atom in common with only one other C–H bond (in $>CH_2$); a tertiary bond is one that is alone (in $\geqslant CH$). A clue to how to improve the systems of bond additivities is provided by comparing, from this point of view, the heats of atomization of isomers. Thus in neopentane, in which all the C–H bonds are primary bonds, the heat of atomization is appreciably greater than that in the normal and iso compounds, and this suggests that primary bonds are stronger than secondary and tertiary ones; a similar conclusion can be drawn from the results for the two butanes.

In the light of this conclusion it is possible to proceed in a more quantitative manner and to arrive at a scheme which represents the heats to a considerably better approximation than does the simple procedure. This improved scheme will be built up on the basis of the following assumptions:

1. The strength of the C–C bond is the same in all of the paraffins; it may be denoted by c_1.

2. The strengths of all primary C–H bonds are the same; the strength may be denoted by p. Similarly the secondary and tertiary bond strengths, s and t, are constants.

There are four quantities, c_1, p, s, and t, to be determined from the data, and four Q_a values are therefore required to determine them. The success of the method depends upon what choice is made, and after the trial of a number of possibilities it was found that the most satisfactory agreement was obtained by using the values for 2,2-dimethylbutane, 3-methylhexane, 2,2-dimethylpentane, and 2,3-dimethylpentane. The data for these compounds give rise to the following equations:

$$5c_1+12p+2s = 1803.9, \quad [4]$$

$$6c_1+9p+6s+t = 2081.3, \quad [5]$$

[6] $$6c_1+12p+4s = 2084.6,$$

[7] $$6c_1+12p+2s+t = 2082.9.$$

The solution of these equations gives

$$c_1 = 85.40 \text{ kcal.}, \qquad s = 97.650 \text{ kcal.},$$

$$p = 98.467 \text{ kcal.}, \qquad t = 96.797 \text{ kcal.}$$

Calculated Q_a values derived on the basis of these figures are shown in the fourth column of Table I, and the agreement is seen to be very satisfactory,

TABLE I

THE c_1–s–p–t SCHEME FOR THE PARAFFINS

c_1(C—C) = 85.40 p (primary C—H) = 98.467
s (secondary C—H) = 97.650 t (tertiary C—H) = 96.797

Paraffin	Bonds	Q_f (obs.)	Q_a (obs.)	Q_a (calc.)	Q_a(calc.) − Q_a(obs.)
Ethane, C_2H_6	c_1+6p	20.2	676.1	676.2	−0.1
Propane, C_3H_8	$2c_1+6p+2s$	24.8	956.6	956.9	−0.3
n-Butane, C_4H_{10}	$3c_1+6p+4s$	30.15	1237.85	1237.6	0.25
Isobutane, C_4H_{10}	$3c_1+9p+2s+t$	32.15	1239.85	1239.2	0.65
n-Pentane, C_5H_{12}	$4c_1+6p+6s$	35.0	1518.6	1518.3	0.3
Isopentane, C_5H_{12}	$4c_1+9p+2s+t$	36.9	1520.5	1519.9	0.6
Neopentane, C_5H_{12}	$4c_1+12p$	39.7	1523.3	1523.2	0.1
n-Hexane, C_6H_{14}	$5c_1+6p+8s$	39.96	1799.5	1799.0	0.5
2-Methylpentane, C_6H_{14}	$5c_1+9p+6s+t$	41.66	1801.2	1800.6	0.6
3-Methylpentane, C_6H_{14}	$5c_1+9p+6s+t$	41.02	1800.5	1800.6	−0.1
2,2-Dimethylbutane, C_6H_{14}	$5c_1+12p+2t$	44.35	1803.9	1803.9	0
2,3-Dimethylbutane, C_6H_{14}	$5c_1+12p+2t$	42.49	1802.0	1802.2	−0.2
n-Heptane, C_7H_{16}	$6c_1+6p+10s$	44.89	2080.2	2079.7	0.5
2-Methylhexane, C_7H_{16}	$6c_1+9p+6s+t$	46.6	2081.9	2081.3	0.6
3-Methylhexane, C_7H_{16}	$6c_1+9p+6s+t$	45.96	2081.3	2081.3	0
3-Ethylpentane, C_7H_{16}	$6c_1+9p+6s+t$	45.34	2080.6	2081.3	−0.7
2,2-Dimethylpentane, C_7H_{16}	$6c_1+12p+4s$	49.3	2084.6	2084.6	0
2,3-Dimethylpentane, C_7H_{16}	$6c_1+12p+2s+2t$	47.6	2082.9	2082.9	0

the errors* being in no case higher than 0.05%. Methane is not included, the C–H bond strength in it, 99.5 kcal., being greater again than that of a primary C–H bond.

In addition to the agreement with the observed Q_a values, the c_1–p–s–t scheme obtained in this way shows a number of other satisfactory and interesting features, as follows.

1. *Regularity of Values*

In the first place, the values for C–H (methane), C–H (p), C–H (s), and C–H (t) diminish in a more or less regular manner. A similar type of decrease in dissociation energies has frequently been invoked to explain the fact that in hydrocarbon chemistry the reactivity of C–H bonds decreases in the order

tertiary > secondary > primary.

Rice (28), for example, found the relative rates of attack of alkyl radicals on

*Greater errors are, however, found with the octanes.

primary, secondary, and tertiary hydrogen atoms to be 1:3:33 at 300°C. A similar conclusion has been reached from studies of the oxidation of hydrocarbons (48).

2. *Relationship with Heats of Dissociation*

The value obtained in the above manner for the C–C bond strength is consistent with that obtained by entirely independent methods for the *dissociation energy* of C–C bonds. Kistiakowsky and co-workers (1, 2, 22, 47) have shown that at 25°C. the heat of dissociation of methane into CH_3+H is ~102 kcal., and from this together with the thermochemical relationships

$$H_2 + C_2H_6 = 2CH_4 + 15.6 \text{ kcal.},$$

$$2H = H_2 + 104.2 \text{ kcal.},$$

it follows that

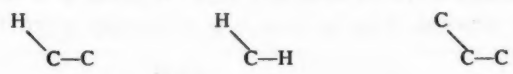
$$C_2H_6 = 2CH_3 - 84.4 \text{ kcal.}$$

This value, which is independent of the value for the heat of sublimation of carbon, is very close to the C–C bond strength obtained above ($c_1 = 85.40$). It is of interest that the c_1 value *is* dependent on the value assumed for the heat of sublimation of carbon; if the value of 125 kcal. were taken for this value, as proposed by some, c_1 would be 55.8 and therefore in considerable disagreement with the value for the heat of dissociation.

An interesting result is obtained when one derives from the present work a value for the heat of sublimation of diamond. Diamond can be considered to be an extended paraffin hydrocarbon, containing only C–C bonds, and the heat of sublimation of a mole should be the sum of the bond strengths for all of the bonds contained in a mole of carbon atoms. The number of bonds in a mole of diamond is twice the number of carbon atoms, so that the energy of sublimation should be $2\times85.40 = 170.8$ kcal. The experimental value is 171.2 kcal., in excellent agreement. No such agreement is obtained if bond strengths are calculated on the basis of other values for the heat of sublimation of graphite. Thus if the heats of atomization of all the paraffins had been calculated using the 125 kcal. value, the C–C bond strength (c_1) would have been 55.8 kcal. This leads to a heat of sublimation of diamond of $2\times55.8 = 111.6$ kcal., to be compared with the value for diamond of about 125 kcal. which must be assumed if the 125 value is taken for graphite.* This argument would appear to provide some evidence in favor of the 171 kcal. value.

3. *The Scheme of Near-neighbor Interactions*

It is now of interest to see how the scheme proposed is related to an alternative scheme that has some quantum-mechanical justification (9, 12), namely a scheme that takes into account interactions between bonds that spring from a common carbon atom. In the paraffins there are three different kinds of such interactions, and these may be denoted by *a*, *b*, and *c* as follows:

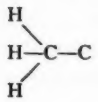


a *b* *c*

**The heat of sublimation of graphite is actually 0.45 kcal. greater than that of diamond.*

It would clearly be possible to attempt a scheme of bond strengths by assigning basic values g and h to the C–C and C–H bonds, respectively, and adding correction terms according to the numbers of interactions of the types a, b, and c. Such a scheme will be referred to as the g–h–a–b–c system.

Now it is readily seen that whenever there is a triplet of primary bonds, i.e. whenever the structure



exists, there are three interaction terms of type a, three of type b, and none of type c. Thus we have

$$3p = 3h+3a+3b. \quad [8]$$

In a similar manner it can be seen that

$$2s = 2h+4a+b+c \quad [9]$$

and

$$t = h+3a+3c. \quad [10]$$

These equations can be used to relate the c_1–s–p–t system to the g–h–a–b–c system. For example 3-methylpentane may be represented by either

$$5c_1+9p+4s+t$$

or

$$5g+14h+20a+11b+5c,$$

these alternative formulations being rendered equivalent by equations [8], [9], and [10].

It follows that there is no real difference between the two schemes, and that the c_1–s–p–t one is entirely consistent with the hypothesis that near-neighbor interactions are the only ones that need be considered. For practical purposes the c_1–s–p–t system is to be preferred, for various reasons. It is simpler to use, not only because it has one fewer parameter (four instead of five), but because it is easier to count bond types than bond interactions. Furthermore, if the g–h–a–b–c system is used one of the values must be assigned entirely arbitrarily. That this is so may be seen by inserting into eqs. [8], [9], and [10] the p, s, and t values obtained earlier, and attempting to solve for h, a, b, and c. Since there are three equations and four unknowns this cannot be done, but one can arrive at the solutions

$$c = -0.018,$$

$$2a-b = -1.616.$$

One may assign a purely arbitrary value to either a or b, after which it is possible to proceed. Suppose that b is arbitrarily given the value zero; it follows that

$$a = -0.808.$$

One finds that

$$h = 99.275.$$

The conclusion is that a g–h–a–b–c scheme with the values

$$g = 85.40, \qquad a = -0.808,$$
$$h = 99.275, \qquad b = 0,$$
$$c = -0.018$$

(or indeed an infinite number of other schemes with a or b chosen arbitrarily) is equivalent to the c_1–p–s–t scheme proposed above, and will give exactly the same predictions for the heats of atomization of the paraffins.

The Olefins

The unsaturated hydrocarbons can be treated in a somewhat similar manner. After trials of various possibilities it has been found that the most satisfactory procedure for the olefins is to classify carbon–hydrogen bonds as follows:

(1) Bonds that are neither next to, nor next but one to, a double bond; these are considered to be ordinary primary, secondary, and tertiary bonds and to have the bond strengths calculated above for the paraffins.

(2) Bonds that are next but one to a double bond; these may be primary, secondary, or tertiary bonds, and their strengths are denoted as p', s', and t'.

(3) Bonds that are next to a double bond; these may be secondary or tertiary and their strengths will be denoted as s_2 and t_2. The carbon–carbon single bond strength (c_1) is assumed to be the same as previously determined; the carbon–carbon double-bond strength will be denoted as c_2.

In order to determine the additional bond strengths c_2, p', s', t', s_2, and t_2, the following heats of atomization were chosen:

(1) 3-Methyl-1-butene
$3c_1+c_2+6p+2s_2+t_2+t' = 1386.3$

(2) 2-Methyl-2-butene
$3c_1+c_2+t_2+9p' = 1389.6$

(3) 2-Methyl-1-butene
$3c_1+c_2+3p+2s_2+3p'+2s' = 1388.1$

(4) 4-Methyl-1-pentene
$4c_1+c_2+6p+t+2s_2+t_2+2s' = 1667.0$

(5) 2-Ethyl-1-butene
$4c_1+c_2+6p+2s_2+4s' = 1668.2$

(6) 3,3-Dimethyl-1-butene
$4c_1+c_2+9p+2s_2+t_2 = 1669.6$

With the values obtained earlier for c_1, p, s, and t, these equations give rise to the figures given in Table II. In Table III are shown calculated and observed values for a large number of olefins; the agreement is seen to be very satisfactory.

TABLE II

BOND STRENGTHS FOR C—C AND C—H BONDS

$c_1 = 85.40$	$p = 98.467$	$p' = 98.902$	
$c_2 = 145.275$	$s = 97.650$	$s' = 98.002$	$s_2 = 99.2575$
	$t = 96.797$	$t' = 97.483$	$t_2 = 98.007$

TABLE III

CALCULATED AND OBSERVED HEATS OF ATOMIZATION FOR OLEFINS

Compound	Bonds	Q_f (obs.)	Q_a (obs.)	Q_a (calc.)
Ethylene	c_2+4s_2	−12.50	539.3	542.3
Propylene	$c_1+c_2+t_2+2s_2+3p'$	− 4.88	822.8	823.9
1-Butene	$2c_1+c_2+t_2+2s_2+2s'+3p$	+ 0.03	1103.6	1104.0
cis-2-Butene	$2c_1+c_2+2t_2+6p'$	1.67	1105.2	1105.5
trans-2-Butene		2.67	1106.2	1105.5
2-Methylpropene	$2c_1+c_2+2s_2+6p'$	4.04	1107.5	1108.0
1-Pentene	$3c_1+c_2+t_2+2s_2+2s'+2s+3p$	5.00	1384.4	1384.7
cis-2-Pentene	$3c_1+c_2+2t_2+2s'+3p'+3p$	6.71	1386.1	1387.4
trans-2-Pentene		7.59	1387.0	1387.4
2-Methyl-1-butene	$3c_1+c_2+2s_2+2s'+3p'+3p$	8.68	1388.1	1388.1
3-Methyl-1-butene	$3c_1+c_2+t_2+t'+2s_2+6p$	6.92	1386.3	1386.3
2-Methyl-2-butene	$3c_1+c_2+t_2+9p'$	10.17	1389.6	1389.6
1-Hexene	$4c_1+c_2+t_2+2s_2+2s'+4s+3p$	9.96	1665.3	1665.4
cis-2-Hexene	$4c_1+c_2+2t_2+2s'+2s+3p'+3p$	11.56	1666.9	1666.3
trans-2-Hexene		12.56	1667.9	1666.3
cis-3-Hexene	$4c_1+c_2+2t_2+4s'+6p$	11.56	1666.9	1665.7
trans-3-Hexene		12.56	1667.9	1665.7
2-Methyl-1-pentene	$4c_1+c_2+2s_2+2s'+2s+3p+3p'$	13.56	1668.9	1668.8
3-Methyl-1-pentene	$4c_1+c_2+t_2+t'+2s_2+2s+6p$	11.02	1666.4	1667.2
4-Methyl-1-pentene	$4c_1+c_2+t_2+t+2s_2+2s'+6p$	11.66	1667.0	1667.0
2-Methyl-2-pentene	$4c_1+c_2+t_2+2s'+6p'+3p$	14.96	1670.3	1667.0
cis-3-Methyl-2-pentene	$4c_1+c_2+t_2+2s'+6p'+3p$	14.32	1669.6	1669.7
trans-3-Methyl-2-pentene		14.32	1669.6	1669.7
cis-4-Methyl-2-pentene	$4c_1+c_2+2t_2+t'+3p'+6p$	13.26	1668.6	1667.9
trans-4-Methyl-2-pentene		14.26	1669.6	1667.9
2-Ethyl-1-butene	$4c_1+c_2+2s_2+4s+6p$	12.92	1668.2	1668.2
2,3-Dimethyl-1-butene	$4c_1+c_2+2s_2+t'+3p'+6p$	14.78	1670.1	1670.4
3,3-Dimethyl-1-butene	$4c_1+c_2+2s_2+t_2+9p$	14.25	1669.6	1669.6
2,3-Dimethyl-2-butene	$4c_1+c_2+12p'$	15.91	1671.2	1673.7

TABLE IV

ACETYLENIC COMPOUNDS

Compound	Bonds	Q_f (obs.)	Q_a (obs.)	Q_a (calc.)	Q_a(calc.) − Q_a(obs.)
Acetylene, $CH{\equiv}CH$	c_3+2t_3	−54.2	393.4	394.9	1.5
Methylacetylene, $CH_3C{\equiv}CH$	$c_3+c_1+t_3+3p$	−44.3	679.2	679.4	0.2
Ethylacetylene $C_2H_5{\equiv}CH$	$c_3+2c_1+t_3+2s+3p$	−39.7	959.6	960.1	0.5
Dimethylacetylene, $CH_3C{\equiv}CH_3$	c_3+2c_1+6p	−35.4	963.9	963.9	0
Propylacetylene, $C_3H_7C{\equiv}CH$	$c_3+3c_1+t_3+4s+3p$	−34.5	1240.7	1240.8	0.1
Methylethylacetylene, $CH_3C{\equiv}CC_2H_5$	$c_3+3c_1+2s+6p$	−30.8	1244.4	1244.6	0.6
Isopropylacetylene $CH_3CH(CH_3)C{\equiv}CH$	$c_3+3c_1+t_3+6p+t$	−32.6	1242.6	1242.4	−0.2
n-Butylacetylene $C_4H_9C{\equiv}CH$	$c_3+4c_1+t_3+6s+3p$	−29.6	1521.5	1521.5	0
n-Pentylacetylene, $C_5H_{11}C{\equiv}CH$	$c_3+5c_1+t_3+8s+3p$	−24.6	1802.4	1802.2	−0.2
n-Hexylacetylene, $C_6H_{13}C{\equiv}CH$	$c_3+6c_1+t_3+10s+3p$	−19.7	2083.2	2082.9	−0.3
n-Heptylacetylene, $C_7H_{15}C{\equiv}CH$	$c_3+7c_1+t_3+12s+3p$	−14.8	2363.9	2363.6	−0.3

It may be seen that one source of minor error in the treatment arises from the neglect of forces between non-bonded atoms. That these forces are significant is illustrated by the differences in heats of atomization between *cis* and *trans* isomers; thus *cis*-2-pentene and *trans*-2-pentene, although having identical bond systems, have heats differing by 0.9 kcal. Generally the *trans* compound has the higher value, but the 3-methyl-2-pentenes (see Table III) constitute an exception.

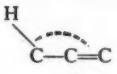
Relationship to a Scheme of Interactions

It is now of interest to see how the scheme proposed is related to an interaction scheme. The double bond introduces the two following additional neighboring-bond interactions:

d

e

Since, moreover, bonds next but one to a double bond are found to be slightly different from *p*, *s*, and *t* bonds, it is clear that the interaction



f

is also involved. The following relationships are then obtained:

[11] $$t_2 = h+a+e+d,$$

[12] $$2s_2 = 2h+b+2e,$$

[13] $$3p' = 3h+3a+3b+3f,$$

[14] $$2s' = 2h+4a+b+c+2f,$$

[15] $$t' = h+3a+3c+f.$$

Insertion into eqs. [11] and [12] of the known values of t_2, s_2, h, a, and b gives rise to

$$d = -0.4425, \qquad e = -0.0175.$$

Insertion into eq. [13] of the values of p', h, a, and b gives rise to

$$f = 0.435.$$

A similar treatment of eqs. [14] and [15] gives values for f of 0.343 and 0.632. Equations [13], [14], and [15] are not exactly compatible, but are nearly so, and a slightly different set of values for p', s', and t' would lead to equal values of f. The scheme proposed is therefore very closely similar to (but is much simpler than) an interaction scheme of the type indicated.

It is of interest that whereas the interactions c, d, and e (and perhaps a and b also) are all negative, the f interaction is positive; this is of course related to the fact that C–H bonds are slightly strengthened by being next but one to double bonds.

The Acetylenes

Column 2 of Table IV lists heats of formation for a number of acetylenes, and these have been converted into heats of atomization in column 3.

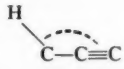
The best agreement was obtained by using the following values:

$$c_3 \text{ (the C}\equiv\text{C bond strength)} = 202.3 \text{ kcal.},$$

t_2 (the strength of a C–H bond adjacent to a triple bond) = 96.3 kcal.

The Q_a values calculated on this basis are shown in the fourth column. It was found that no advantage was gained by employing special values for C–H bonds next but one to the triple bond; the regular p, s, and t values are used for these.

This scheme is evidently equivalent to one of neighboring-bond interactions, the next-near-neighbor interaction



being taken to be zero. The interaction term corresponding to

$$\text{H—C}\equiv\text{C}$$

is $96.3-99.275 = -2.975$ kcal.

Aromatic Compounds

Observed heats of formation and of atomization of aromatic compounds are shown in Table V. In the fourth column are given heats of atomization

TABLE V

AROMATIC COMPOUNDS

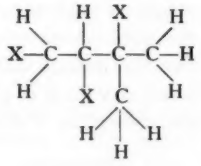
Compound	Bonds	Q_f	Q_a (obs.)	Q_a (calc.)	Q_a(calc.) $-Q_a$(obs.)
Benzene, C_6H_6	$3c_1+3c_2+6t_2$	−19.8	1322.9	1280.1	42.8
Toluene, $CH_3C_6H_5$	$4c_1+3c_2+5t_2+3p'$	−11.9	1606.7	1564.2	42.5
Ethylbenzene, $C_2H_5C_6H_5$	$5c_1+3c_2+5t_2+2s_1+3p$	−7.1	1887.4	1844.3	43.1
o-Xylene, $(CH_3)_2C_6H_4$	$5c_1+3c_2+4t_2+6p'$	−4.5	1890.0	1848.3	41.7
m-Xylene, $(CH_3)_2C_6H_4$	$5c_1+3c_2+4t_2+6p'$	−4.1	1890.4	1848.3	42.1
p-Xylene, $(CH_3)_2C_6H_4$	$5c_1+3c_2+4t_2+6p'$	−4.3	1890.2	1848.3	41.9
n-Propylbenzene, $C_3H_7C_6H_5$	$6c_1+3c_2+2s'+2s+3p+5t_2$	−1.9	2168.5	2125.0	43.5
Isopropylbenzene, $C_3H_7C_6H_5$	$6c_1+3c_2+5t_2+6p+t'$	−0.9	2169.5	2126.5	43.0
1-Methyl-2-ethylbenzene, $CH_3(C_2H_5)C_6H_4$	$6c_1+3c_2+4t_2+2s'+3p+3p'$	−0.3	2170.1	2128.4	41.7
1-Methyl-3-ethylbenzene, $CH_3(C_2H_5)C_6H_4$	$6c_1+3c_2+4t_2+2s'+3p+3p'$	−0.5	2170.9	2128.4	42.5
1-Methyl-4-ethylbenzene, $CH_3(C_2H_5)C_6H_4$	$6c_1+3c_2+4t_2+2s'+3p+3p'$	0.8	2171.2	2128.4	42.8
1,2,3-Trimethylbenzene, $(CH_3)_3C_6H_3$	$6c_1+3c_2+3t_2+9p'$	2.3	2172.7	2132.4	40.6
1,2,4-Trimethylbenzene, $(CH_3)_3C_6H_3$	$6c_1+3c_2+3t_2+9p'$	3.3	2173.7	2132.4	41.3
1,3,5-Trimethylbenzene, $(CH_3)_3C_6H_3$	$6c_1+3c_2+3t_2+9p'$	3.8	2174.2	2132.4	41.8
					Av. = 42.2

calculated without regard to resonance energy, i.e., by treating the double bonds in the benzene ring as ordinary double bonds. The differences between the observed and calculated values are listed in the last column, and are seen to be quite constant. The average value of these differences is 42.2 kcal., and this can be taken to be the resonance energy, the value of which should be subtracted when it is desired to estimate the heats of atomization or formation of benzene derivatives.

Compounds Containing Specific Groups

It is now necessary to consider the situation when hydrogen atoms in the hydrocarbons are replaced by specific groups, such as aldehyde, alcohol, and nitrate groups. This type of compound cannot, in principle, be treated in as simple a manner as previously, and unfortunately a completely satisfactory system of bond energies cannot as yet be worked out. This is because there do not exist, in the case of compounds containing specific groups, data for a sufficient number of homologous compounds. It is, however, of interest to consider a general type of treatment that it will ultimately be possible to test using adequate data. Two situations may be considered; the one in which there is no more than one of the specific groups X on any carbon atom, and the one in which more than one group is present. The latter situation is more complex in that interactions of the type X—C—X must be considered.

1. When there is never more than one X on each carbon atom, as in the compound



it may be seen that as far as neighbor interactions are concerned all possible structural features of the compound are included in a scheme that recognizes three different types of C–X bonds:

(*a*) bonds in which X replaces a primary hydrogen atom; these may be designated x^p bonds;

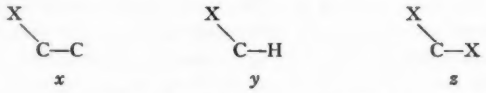
(*b*) x^s bonds, in which a secondary hydrogen atom is replaced; and

(*c*) x^t bonds, involving a tertiary hydrogen.

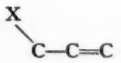
Since the values of c_1, p, s, t, etc., have been determined from the hydrocarbon data, it would be possible to evaluate x^p, x^s, and x^t from the data for those members of a homologous series of this type, and to test the system on additional members of the series. For an adequate test it would be desirable to have data for at least 10 compounds, and the data should be accurate to within 0.2 kcal. or so. Neither of these conditions can as yet be satisfied for any group X.

2. When more than one X can be on a carbon atom the simplest scheme taking into account neighbor interactions would be one in which they are

treated explicitly. A theory of this type would proceed as follows. The additional interaction terms are



with more being necessary if there are double or triple bonds; in the former case it would probably be desirable to add terms for the next-near-neighbor interaction



The interaction terms a, b, c, d, and e have already been calculated from the hydrocarbon data, and results for these compounds containing C–X bonds would enable x, y, and z to be determined. Again this cannot as yet be done for lack of adequate data.

In view of the fact that data do not permit a treatment equivalent to that for the hydrocarbons the best that can at present be done is to treat all C–X bonds as equivalent, and be content with bond strengths that are an average of values showing some scatter. For most practical purposes this procedure is in fact adequate, since most compounds of interest contain only a few C–X bonds; the errors therefore do not tend to accumulate in the way they do with C–H bonds.

This procedure has been applied to a number of different groups, and the contributions of various groups to the energy of atomization have been evaluated. Since the data for substances other than the hydrocarbons are not very accurate or extensive the details will not be given here. A note on the sources of the thermochemical values is given in the Appendix, and the final group contributions are shown in Table VI. The procedure used in

TABLE VI

RECOMMENDED CONTRIBUTIONS FOR SPECIFIC GROUPS

Bond	Contribution to heat of atomization, kcal.
C—OH (alcohol)	198.1
C—O—C (ether)	172.0
C—CHO (aldehyde)	355.4
C—CO—C (ketone)	350.1
C—COOH (acid)	480.1
C—NH_2 (amine)	256.6
C—NO_2 (nitro)	285.2
C—ONO_2 (nitrate)	354.5

deciding the type of a C–H bond is to treat the substituent as if it were a carbon atom; in ethyl alcohol, for example, it is considered that there are three primary C–H bonds and two secondaries. An alternative procedure would be to consider all five to be primaries, since the molecule is derived from ethane, which has six primaries. The procedure employed seems to give a smaller spread of values.

There is a great need for additional work on series of homologous compounds, and the values given in Table VI will require revision as new data accumulate.

HEATS OF VAPORIZATION

The bond contributions arrived at in the previous section enable an estimate to be made of the heats of atomization of gases and, by an extension to be discussed later, of the heats of formation and combustion of gases. It is clearly of some practical importance to be able to extend this system to liquids and solids. In the present section a start has been made on this problem for the case of liquids; for solids a satisfactory solution will probably have to await further experimental results.

The procedure that has been adopted is to analyze data for heats of vaporization and to arrive at a scheme of bond energies of the same type as that used for heats of atomization. It is then a simple matter to combine the two systems and so obtain a scheme of bond energies for liquids; this is done in the section that follows.

It is actually found that heats of vaporization are not strictly additive in terms of bonds, and that for best agreement the presence of certain structural features (such as five–carbon structures of the neopentane type) should be taken into account. However the simple system of bond energies is, as will be seen, very satisfactory, and is certainly adequate for present purposes. Since heats of vaporization are relatively small compared with heats of atomization and combustion (and sometimes with heats of formation) a large percentage error in a heat of vaporization will lead to only small errors in the final estimated values.

Paraffins

Accurate values for a number of paraffins are given in the N. B. S. tables (46), and some of them are shown in the second column of figures in Table VII. Analysis of these values reveals the fact that it is possible to make

TABLE VII

CALCULATED AND OBSERVED HEATS OF VAPORIZATION FOR PARAFFINS

Paraffin	Heat of vaporization (kcal. per mole)		Difference (calc. − obs.)
	Obs.	Calc.	
n-Hexane	7.540	7.596	0.056
2-Methylpropane	4.570	4.967	0.397
2-Methylbutane	5.878	6.125	0.247
2-Methylpentane	7.138	7.186	0.048
2-Methylhexane	8.318	8.444	0.126
2-Methylheptane	9.483	9.602	0.119
2-Methyloctane	10.670	10.760	0.090
3-Ethylpentane	8.419	8.441	0.022
3-Ethylhexane	9.475	9.599	0.124
3-Ethylheptane	10.710	10.757	0.047
2,2-Dimethylpropane	5.200	5.932	0.732
2,2-Dimethylbutane	6.617	7.080	0.363
2,2-Dimethylpentane	7.751	8.238	0.487
2,2-Dimethylhexane	8.912	9.396	0.484
2,2-Dimethylheptane	10.100	10.554	0.454

reasonable estimates of them using the following values for the contributions of the various bonds:

$$c_1 = 0 \text{ kcal.}, \qquad s = 0.579 \text{ kcal.},$$

$$p = 0.494 \text{ kcal.}, \qquad t = 0.518 \text{ kcal.}$$

Table VII shows calculated values and the differences between calculated and observed. The agreement is seen to be reasonably satisfactory in most cases, but is least so in hydrocarbons having the neopentane type of structure; such compounds have heats of vaporization that are significantly lower than the predicted ones, a fact that may be related to their high degree of symmetry. In estimating the values for compounds containing this structural feature it would be well to subtract a value of about 0.5.

The data for unsaturated hydrocarbons are unfortunately not adequate to allow a similar treatment to be applied to them.

Compounds Containing Specific Groups

Heat of vaporization data for compounds such as alcohols, ethers, and acids are not extensive and not of great accuracy. Application of the same type of treatment as the above, however, leads to the conclusion that to a useful approximation the values are additive. This is illustrated by the results shown in Table VIII for the nitrates; the data for these are fairly reliable (see Appendix). The details for other groups will not be given, but the thermochemical data employed are discussed in the Appendix and the final group contributions are summarized in Table IX.

TABLE VIII

HEATS OF VAPORIZATION OF NITRATES

Nitrate	Q_v (obs.)	C—ONO_2
CH_3ONO_2	8.2	6.72
$C_2H_5ONO_2$	8.7	6.06
CH_2ONO_2 | CH_2ONO_2	15.7	6.69
CH_2ONO_2 | $CHONO_2$ | CH_2ONO_2	21.7	6.29
		Av. 6.44

Improvement for all of these compounds could no doubt be achieved by employing a procedure such as that used by Wiener (50), who introduces parameters that take some account of the general shape of the molecule. However for present purposes it is more useful to have a system that is of the same type as that used for heats of atomization—i.e. involving only bond contributions. With such a system for heats of vaporization it is then possible,

as will now be explained, to arrive at a scheme for making predictions of the thermochemical values for liquids.

TABLE IX

BOND CONTRIBUTIONS TO HEATS OF VAPORIZATION

Bonds	Contribution (kcal. per mole)
C—C	0
C—H (*p*)	0.494
C—H (*s*)	0.579
C—H (*t*)	0.518
C—OH	6.76
C—CHO	5.21*
C—CO—C	6.76
C—O—C	1.25
C—COOH	18.8*
C—ONO_2	6.44
C—NO_2	7.04

**Based on one heat of vaporization only; data from Ref. (55).*

TABLE X

BOND CONTRIBUTIONS FOR HEATS OF ATOMIZATION, FORMATION, AND COMBUSTION OF GASES AND LIQUIDS

Bond	Symbol	Heat of atomization		Heat of formation		Heat of combustion	
		Gas	Liquid	Gas	Liquid	Gas	Liquid
C—C	c_1	85.4	85.4	−0.45	−0.45	47.48	47.48
C=C	c_2	145.3	(145.3)	30.2	(30.2)	32.5	(32.5)
C≡C	c_3	202.3	(202.3)	−55.3	(−55.3)	196.3	(196.3)
C—H	p	98.47	98.96	3.45	3.95	54.22	53.73
C—H	s	97.65	98.23	2.64	3.21	55.04	54.46
C—H	t	96.80	97.32	1.78	2.30	55.89	55.37
C—H	p'	98.90	(99.40)	3.89	(4.38)	53.79	(53.29)
C—H	s'	98.00	(97.58)	2.99	(3.57)	54.69	(54.11)
C—H	t'	97.48	(98.00)	2.47	(2.99)	55.20	(54.69)
C—H	s_2	99.26	(99.84)	−10.07	(−9.49)	75.58	(75.00)
C—H	t_2	98.01	(98.53)	−25.62	(−24.11)	98.97	(98.45)
C—H	t_3	96.30	(96.82)	1.29	(1.80)	56.39	(55.87)
C—OH	a_{1c}	198.1	204.9	49.93	50.69	13.75	6.99
C—O—C	e	172.0	173.3	27.0	28.3	20.0	18.7
C—CHO	a_{1d}	355.4	360.6	29.5	34.7	122.2	117.0
C—CO—C	k	350.1	356.9	33.4	40.2	107.7	100.9
C—COOH	a_e	480.1	498.6	95.1	113.9	56.7	37.9
C—NH_2	a_m	256.6	—	−3.5	—	95.3	—
C—NO_2	n_i	285.2	292.2	11.0	18.0	12.6	5.5
C—ONO_2	n_a	354.5	361.0	21.1	27.5	2.4	−4.0
C—$NHNO_2$	n_{m1}	—	440.2	—	0.9	—	56.8
C>C—NNO_2	n_{m2}	—	421.3	—	−8.9	—	55.9

The values in brackets are based on the assumption that the contributions for the heats of vaporization of C—H are the same irrespective of the proximity of double and triple bonds.

HEATS OF FORMATION AND COMBUSTION OF GASES AND LIQUIDS

In the present section the results of the previous work will be consolidated and an outline will be given of a complete set of procedures for estimating heats of atomization, formation, and combustion of both gases and liquids.

Table X shows the final bond contributions that have been arrived at. The methods used in obtaining them will now be discussed.

Heats of Atomization

The first column of numbers in the table consists of the values obtained earlier. The second shows the corresponding values for liquids. Since both the heats of atomization and the heats of vaporization are given additively in terms of bond contributions it is necessary simply to add together the two contributions in order to obtain that for the heat of atomization of a liquid. For example, the value 361.0 for the nitrate group is the sum of 354.5, the gas contribution, and 6.5, that for the heat of vaporization.

Heats of Formation

The conventional heat of formation is related to the heat of atomization by eq. [1], which involves n_C, n_H, n_O, and n_N, the numbers of the various atoms in the molecule. In order to relate the contributions for heats of formation to those for heats of atomization it is necessary to relate n_C, n_H, n_O, and n_N to the numbers of the various bonds in the molecule.

The following example will illustrate the type of procedure that may be employed for doing this. Consider a molecule containing C_1 carbon–carbon single bonds, C_2 carbon–carbon double bonds, P primary (p) C–H bonds, S secondary (s) C–H bonds, S_2 bonds of type s_2 (next to a double bond), T_2 bonds of type t_2 (next to a double bond), S' bonds of type s', N_a nitrate groups, and A_{ld} aldehyde groups. According to the previous work (see column 1 of Table X) the heat of atomization of such a compound in the gas phase will be

$$[16]\quad Q_a = 85.4\ C_1+145.28\ C_2+98.47\ P+97.65\ S+99.26\ S_2 +98.00\ S' +354.5\ N_a+355.4\ A_{ld}.$$

If n_C, n_H, n_O, and n_N can be expressed in terms of C_1, C_2, P, etc., it will then be possible to express Q_f as a linear function of C_1, C_2, P, etc., with explicit coefficients that will be the relevant bond contributions for the various atoms and groups.

Consider first the number of carbon atoms, n_C, in the molecule under consideration. The presence of a primary C–H bond implies the existence of a carbon atom, but since the carbon atom is tetravalent the bond actually only has a one-fourth share in it;* for each primary C–H one must therefore count only a quarter of a carbon atom. The same argument applies to secondary (and tertiary) C–H bonds, and to bonds next but one to a double bond. We thus find that

$$[17]\quad n_C = \tfrac{1}{4}(P+S+S')+ \ldots .$$

**This is no longer true if the C—C bond is next to a double or triple bond; the correction required for this is considered later.*

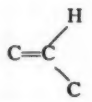
Each C–C single bond has a fourth share in two carbon atoms, so that

[18] $$n_C = \tfrac{1}{4}(P+S+S')+\tfrac{1}{2}C_1+\ldots.$$

Each C–ONO_2 bond has a fourth share in a carbon atom, while each aldehyde group has a fourth share in one carbon atom and a full share in another; thus

[19] $$n_C = \tfrac{1}{4}(P+S+S')+\tfrac{1}{2}C_1+\tfrac{1}{4}N_a+\tfrac{5}{4}A_{id}+\ldots.$$

A slight complication arises from the presence of double (and triple) bonds. Each C=C double bond has one-third share in two carbon atoms, so that the contribution is $\frac{2}{3}C_2$ (for a triple bond it is C_3). An S_2 bond has one-third share in a carbon atom, so that the contribution is $\frac{1}{3}S_2$. Similarly a t_2 bond has a one-third share in a carbon atom, so that a contribution of $\frac{1}{3}T_2$ is indicated. However this result neglects one factor. The existence of a t_2 bond implies the structure*



and this means that an error has been made in treating the C–C single bond, since one end of this is a carbon atom that is only attached to three different atoms. The contribution at one end of the carbon atom is therefore $\frac{1}{3}$ rather than $\frac{1}{4}$, and the estimated number of carbon atoms is therefore too low by $\frac{1}{3}-\frac{1}{4} = \frac{1}{12}$ for every time this structure appears. The easiest way to make the correction is to add a term $\frac{1}{12}T_2$. The final expression for the number of carbon atoms in the molecule is therefore

[20] $$n_c = \tfrac{1}{4}(P+S+S')+\tfrac{1}{2}C_1+\tfrac{2}{3}C_2+\tfrac{1}{3}S_2+(\tfrac{1}{3}+\tfrac{1}{12})T_2+\tfrac{1}{4}N_a+\tfrac{5}{4}A_{id}.$$

Proceeding in a similar manner for the various bonds it is possible to arrive at the coefficients shown in the first column of Table XI. The procedure for the remaining bonds is straightforward except when triple bonds are present. Here again the contributions from C–C single bonds will be wrongly counted unless a correction is made. The number of times the structure

C—C≡C

appears in a molecule is $2C_3-T_3$, and every time it appears the number of carbon atoms is in error by $\frac{1}{4}$; the term $\frac{1}{4}(2C_3-T_3)$ must therefore be added. The expression for n_C for a molecule containing triple bonds therefore contains the terms

[21] $$n_C = C_3+\tfrac{1}{2}T_3+\tfrac{1}{4}(2C_3-T_3)+\ldots.$$

The second column of figures in Table XI shows the corresponding coefficients in the expression for n_H, while the third and fourth are for n_O and n_N. These are obtained in a similar way to the coefficients for n_C.

*A special treatment is required if one of the substituent groups is next to the double bond. There are, however, few data for this type of compound.

TABLE XI

MATRIX OF COEFFICIENTS WHICH RELATE n_C, n_H, n_O, AND n_N TO THE NUMBERS OF BONDS

Bond	n_C	n_H	n_O	n_N
C_1	$\frac{1}{2}$	0	0	0
C_2	$\frac{2}{3}$	0	0	0
C_3	2	0	0	0
P	$\frac{1}{4}$	1	0	0
S	$\frac{1}{4}$	1	0	0
T	$\frac{1}{4}$	1	0	0
P'	$\frac{1}{4}$	1	0	0
S'	$\frac{1}{4}$	1	0	0
T'	$\frac{1}{4}$	1	0	0
S_2	$\frac{1}{3}$	1	0	0
T_2	$\frac{1}{2}$	1	0	0
T_3	$\frac{1}{1}$	1	0	0
A_{1e}	$\frac{1}{4}$	1	1	0
E	$\frac{1}{3}$	0	1	0
A_{1d}	$\frac{5}{4}$	1	1	0
K	$\frac{2}{3}$	0	1	0
A_e	$\frac{5}{4}$	1	2	0
A_m	$\frac{1}{4}$	2	0	1
N_i	$\frac{1}{4}$	0	2	1
N_a	$\frac{1}{4}$	0	3	1
N_{m1}	$\frac{1}{4}$	1	2	2
N_{m2}	$\frac{1}{4}$	0	2	2

In order to obtain the bond contribution to the heat of formation one proceeds as follows. The expression for Q_f contains a number of terms, that for the nitrate group, for example, being as follows:

$$[22] \quad Q_f = Q_a - 171.7\, n_C - 52.09\, n_H - 59.16\, n_O + 113.0\, n_N$$

$$[23] \quad = 354.5\, N_a + \ldots - 171.7\, (\tfrac{1}{4}N_a + \ldots) - 52.09(0 + \ldots) - 59.16(3N_a + \ldots) - 113.0(N_a + \ldots)$$

$$[24] \quad = 21.10\, N_a + \ldots .$$

The entry in the third column of numbers in Table X for the nitrate group is therefore 21.10. The remaining figures are obtained in a similar way.

The values for the liquid state are obtained in the same manner as for the heats of atomization, making use of the heat of vaporization contributions.

Heats of Combustion

The heat of combustion is related to the heat of formation by eq. [2]. The bond contributions to the heats of combustion can therefore be calculated from those for the heats of formation by making use of the appropriate coefficients in Table XI, the procedure being similar to the above. The heat of vaporization contributions must now be *subtracted* from the gas values to obtain those for the liquids.

The resulting contributions are shown in the last two columns of Table X.

SOME EXAMPLES

In order to illustrate the method, and to give some indication of its reliability, typical calculations will now be carried out.

Ethyl Nitrate

The calculation of the heat of combustion of liquid ethyl nitrate is as follows:

$$\begin{aligned} 1 \times c_1 &= 47.48 \\ 3 \times p &= 161.19 \\ 2 \times s &= 108.92 \\ 1 \times n_a &= -4.0 \end{aligned}$$

$$Q_c = 313.59 \text{ kcal.}$$

The observed value, derived from Berthelot's heat of esterification of ethyl nitrate and from Gray's treatment of Wheeler, Whittaker, and Pike's explosion data, is 313.2 kcal.

The heat of formation calculation is, for the liquid:

$$\begin{aligned} 1 \times c_1 &= -0.45 \\ 3 \times p &= 11.85 \\ 2 \times s &= 6.42 \\ 1 \times n_a &= 27.5 \end{aligned}$$

$$Q_f = 45.32 \text{ kcal.}$$

The observed value, based on the data referred to above, is 45.7 kcal.

Diethyl Nitramine

The heat of combustion of liquid diethyl nitramine is calculated as follows:

$$\begin{aligned} 2 \times c_1 &= 94.96 \\ 6 \times p &= 322.38 \\ 4 \times s &= 217.84 \\ 1 \times n_{m2} &= 55.9 \end{aligned}$$

$$Q_c = 691.08 \text{ kcal.}$$

The observed value is 692.2 ± 0.9 kcal.

ACKNOWLEDGMENTS

The author is grateful to Dr. Peter Gray and Mr. Harold Hurwitz for discussions relative to the thermochemistry of the nitrates, and to Dr. Theodore Austin for work on the heats of vaporization. He is also indebted to Miss Susan Pyatt and Mrs. O. Kracek for help with the computations and for valuable suggestions.

APPENDIX. SOURCES OF THERMOCHEMICAL DATA

Hydrocarbons

Q_f and Q_v data were obtained in all cases from the N. B. S. tables (46).

Alcohols

Q_f values for *n*-alcohols up to C_{10} from Rossini (31); other values quoted by Bischowsky and Rossini (6) and by Roberts and Skinner (30).

Q_v values from Landolt-Börnstein (24).

Ethers

Q_f values from Bischowsky and Rossini (6), Kharasch (20), and Stohmann (34). Q_v values calculated from vapor pressure data of Stull (35).

Aldehydes

Q_f values for formaldehyde and acetaldehyde only (46). Q_v values calculated from vapor pressure data of Stull (35).

Ketones

Roberts and Skinner (30) quote Q_f values for CH_3COCH_3, $C_2H_5COCH_3$, *n*-$C_3H_7COCH_3$, and *sec*-$C_3H_7COCH_3$. Q_v values for the first three were calculated from Stull's vapor pressure data (35); Q_f(gas) for the last was obtained using an estimated Q_v. The four Q_f values employed were 51.8, 58.2, 65.1, and 66.8 kcal., respectively.

Acids

Q_f values for HCOOH, CH_3COOH, $CH_2ClCOOH$, and $CHCl_2COOH$ are given by Bischowsky and Rossini (6). A C–Cl value of 80.5 was assumed. Q_v's calculated from Stull's data (35).

Amines

Reliable Q_f data appear to be available only for methylamine and ethylamine (46). No reliable Q_v values.

Nitro Compounds

Thermochemical data for nitro compounds are not of high reliability. Some Q_f values for liquids are given in the Landolt-Börnstein tables (24) and were converted into gaseous values using either experimental heats of vaporization (6) or values estimated using the methods of this paper. Bischowsky and Rossini (6) give Q_v values for nitromethane and nitroethane.

Nitrates

Some of the data for the nitrates are contradictory; discussion of the individual compounds is therefore necessary.

Methyl Nitrate

The value of 29.0 kcal. for Q_f(gas) is based upon a value of Q_f(liquid) = 37.2 kcal. calculated by Gray and Smith (16) from heat of explosion data of Wheeler, Whittaker, and Pike (49), and a heat of vaporization of 8.2 kcal. calculated from vapor pressure measurements of McKinley-McKee and Moelwyn-Hughes (25).

Other sources of data are as follows. Swientoslawski (36) quotes Berthelot as having obtained Q_c(gas) = 166.2, presumably on the basis of the heat of esterification. Using modern thermochemical data this leads to Q_f(liquid) = 39.1. In view of the uncertain origin of this value, however, that of Gray seems

preferable. An alternative determination of Q_v is due to Thompson and Purkis (44), whose results lead to 7.8 kcal. On the whole the McKinley-McKee and Moelwyn-Hughes value seems more reliable; the vapor pressures were measured over a wider temperature range, and the results were fitted to the Antoine equation (Thompson and Purkis report their results only as the equation of a straight line on a log p vs. $1/T$ graph).

Ethyl Nitrate

A value for Q_f(liquid) of 45.7 was calculated by Gray (15) from Wheeler, Whittaker, and Pike's heat of explosion data (49), and the same value is obtained by applying modern auxiliary data to Berthelot's heat of esterification value (5). Thomsen (45) obtained different results by measuring Q_c directly, but the error in this type of investigation is intrinsically greater than in heat of esterification measurements. In view of this, and of the agreement between Berthelot and Gray, their value seems preferable (16*a*).

The vapor pressure of ethyl nitrate was measured by Goodeve (14*a*) over a range of temperature, and a reanalysis of her data leads to a value of $Q_v = 8.7$ at 25°C.

These values lead to Q_f(gas) = 37.0.

Glycol Dinitrate

Rinkenbach (29) and Schmidt (32) give Q_c(liquid) values that both lead to Q_f(liquid) = 58.2. A value of $Q_v = 15.7$ comes from vapor pressure results of Brandner (7); when fitted to the Antoine equation they lead to 15.7 at 25°C. Crater (11) carried out a similar study, but his data lead to a higher Q_v. For various reasons Brandner's results seem more reliable.

Nitroglycerine

A Q_f(liquid) value of 89.0 is calculated from Taylor and Hall's value (41) of 364 for Q_c(liquid). A variety of earlier values have been given in the literature, and Taylor and Hall list objections to these, based mainly on defects in experimental procedures or on absence of information.

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THE FORMATION OF SUPERCOOLED LIQUID SOLUTIONS IN SIMPLE-EUTECTIC TYPE ORGANIC SYSTEMS BY THE SUBLIMATION OF SOLID MIXTURES[1]

By Ralph H. Petrucci[2] and C. H. Sorum[3]

ABSTRACT

A process is described for the formation of supercooled liquid solutions by the sublimation of solid mixtures—the liquids formed being supercooled in the sense that they can be condensed from the vapor phase above solid mixtures at temperatures below the eutectic values. The process can be thought of as proceeding, solids → mixed vapor → supercooled liquid solutions. The general nature of this phenomenon in organic systems of the simple-eutectic type is established as a result of the microscopic and macroscopic experiments performed in this investigation. A $P/T/c$ space-model of a typical binary, eutectic-type, organic system, *o*-nitrophenol–naphthalene, is presented. A physical picture of the process under consideration is made possible on the basis of this model.

INTRODUCTION

In an earlier contribution from this laboratory, Sorum and Durand (4) reported the fact that individual crystals, maintained out of physical contact, could melt at temperatures just slightly above their eutectic temperature as a result of the condensation of the vapor phase above them. Forty-five organic, binary, eutectic-type systems were studied at that time and this phenomenon was observed in every case.

In the present work it was noted that condensation to liquids occurred even when solids were maintained at temperatures below their eutectics. In order that liquids might condense it was necessary to have the collecting surfaces at temperatures below those of the solids; the entire systems therefore were at temperatures below the eutectic values. The liquids formed under these conditions were supercooled solutions of the two components; the evidence of supercooling was the fact that these liquids persisted at temperatures below the eutectics. The present paper is concerned with some of the factors involved in the formation of supercooled liquids by this process.

EXPERIMENTAL

A. Materials

All the chemicals used in this investigation were organic compounds of relatively low melting points and high vapor pressures (*ca.* 10^{-4} to 10^{-1} mm.). The compounds were recrystallized twice from suitable solvents, dried for one to two days over appropriate desiccants in a vacuum desiccator, and then further dried at elevated temperatures and reduced pressures in an Abderhalden Drying Apparatus. The melting points and melting point ranges of the final products were used as criteria of purity.

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin.
[2]*Morley Chemical Laboratory, Western Reserve University, Cleveland, Ohio.*
[3]*Department of Chemistry, University of Wisconsin, Madison, Wisconsin.*

B. Apparatus for Microscopic Experiments

A Bausch and Lomb crystallographic microscope, equipped with 8 and 16 mm. objectives and 7.5 and 10× eyepieces, was used for all the microscopic work. Heating and thermostating of samples were accomplished by the use of a water-heated microscope hot-stage fabricated from aluminum metal. A small water bath equipped with heaters, cooling coils, bimetallic thermoregulator, and circulating pump served as a source of water. The stage could be thermostated with a precision of a few tenths °C. By continuously varying the temperature of the external bath, heating and cooling rates from 0.1° to 1.0°C. per minute could be established. Accurately calibrated mercury-in-glass thermometers inserted through a re-entrant thermometer well were used for making temperature measurements in the stage. A set of inserts fitting into the central light orifice made the stage adaptable for all of the various microscopic measurements—melting points, eutectic temperatures, refractive indices, sublimation temperatures, etc.

C. Macroscopic Sublimation Apparatus

Macroscopic studies on the condensation of liquid sublimate from the vapor phase above solid mixtures were carried out in an all-glass sublimation apparatus. The essential features of this apparatus were sublimation wells to hold the solid samples and "cold-thumb" condensers (maintained at a short distance above the solids) upon which sublimate could condense.

Macroscopic sublimation studies were performed on the system *o*-nitrophenol–naphthalene. Solid mechanical mixtures of the two components were placed in the sublimation wells of the sublimation apparatus and thermostated at one temperature. By maintaining the "cold-thumb" condensers of the apparatus at some lower temperature, liquid condensates were collected on the condensers. Collection of the condensates was allowed to continue for a few days and when sufficient amounts of liquid had deposited (*ca.* 0.01–0.05 ml.) these liquids were analyzed by a microscopic refractometric method.

D. Determination of Eutectic Temperatures

The eutectic temperature for a multicomponent system is the equilibrium temperature at which all the phases, solid, liquid, and vapor, are present in bulk. In practice to initiate and maintain a finite rate of freezing the temperature of a system must be somewhat below the eutectic temperature. To initiate and maintain melting the temperature must be slightly above the eutectic. The true eutectic temperature is somewhere between these upper and lower limits. For the purposes of this paper the melting temperature has been taken as essentially equal to the equilibrium temperature.

Two microscopic methods were used in establishing eutectic temperatures. One was the "contact-method" developed by the Koflers (2). The second method simply involved crystallizing liquid samples between 12- and 25-mm. microscope cover glasses and then observing the lowest temperature at which fusion occurred when these samples were slowly reheated. In contrast to the "contact-method" where eutectic fusion occurred only in a limited "zone-of-mixing" of the components, with the "fusion-preparations" eutectic fusion

could take place anywhere in the crystalline area. The latter method proved to be particularly applicable to studies on ternary and quaternary systems where "zones-of-mixing" of all the components were difficult to establish.

E. Refractive Index Measurements

Mixtures of *o*-nitrophenol and naphthalene were analyzed by determining the refractive indices of solutions of the two components. A series of "working-curves" was established, giving the temperatures at which mixtures of fixed composition had specified refractive indices. Compositions of unknown mixtures were obtained by referring to these standard curves. This method is described in detail by the Koflers (2). Refractive index curves for the system *o*-nitrophenol–naphthalene are presented in Fig. 1.

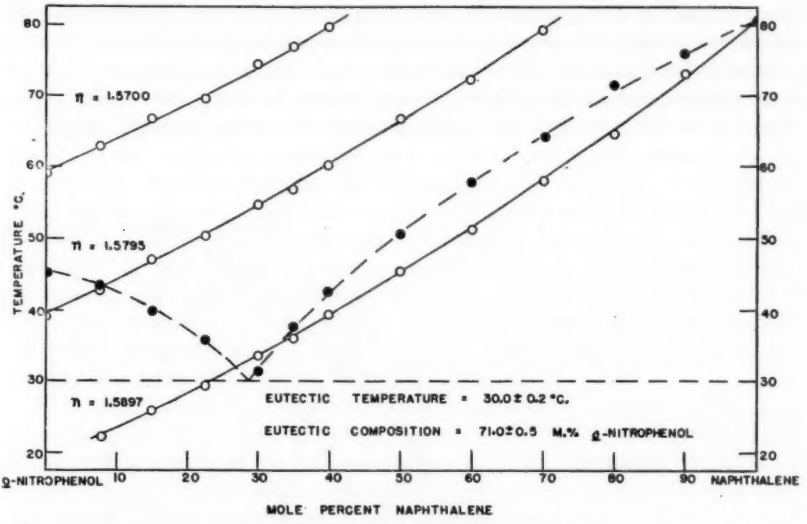

FIG. 1. Equilibrium diagram (closed circles) and refractive index curves (open circles) for the system *o*-nitrophenol–naphthalene.

STUDIES ON THE SYSTEM *o*-NITROPHENOL–NAPHTHALENE

A. Determination of the Equilibrium Diagram

The equilibrium diagram for the system, *o*-nitrophenol–naphthalene, was determined by a combination of macroscopic and microscopic methods. The macroscopic method used was essentially the "thaw-point" method of Rheinboldt (3). In this procedure synthetic solid mixtures are prepared and the melting of such samples followed in a conventional capillary melting-point type of apparatus. The pertinent data are the "beginning melting point" and the "end melting point". In this system the "beginning melting point" for every sample was the eutectic temperature. The "end melting point" corresponded to the primary crystallization temperature in a cooling curve study on a binary system. The synthetic mixtures required were obtained by

melting together weighed amounts of the two components sufficient to give a solution of a few milliliters volume. These solutions were then crystallized and carefully pulverized in a cold mortar. The resulting solid mixtures were used for the melting point determinations. Microscopic melting points were also determined on samples prepared in this same manner.

The equilibrium diagram for the system, *o*-nitrophenol–naphthalene, based on macroscopic melting points is presented in Fig. 1. Equilibrium relationships are shown by dashed lines. Refractive index curves for the system, plotted on the same temperature and composition scales, are given as solid lines.

B. Subeutectic Region of the P/T/c Space-model

The space-model (see Fig. 2) for this system was calculated principally from literature data, although two items of experimental information from this investigation, the eutectic temperature and eutectic composition, were also required. In Fig. 2 the curve *LK* is the vapor pressure curve for pure solid naphthalene and *JI* the vapor pressure curve for pure solid *o*-nitrophenol. The curves *HN* and *GM* define the sum of the vapor pressures of the two

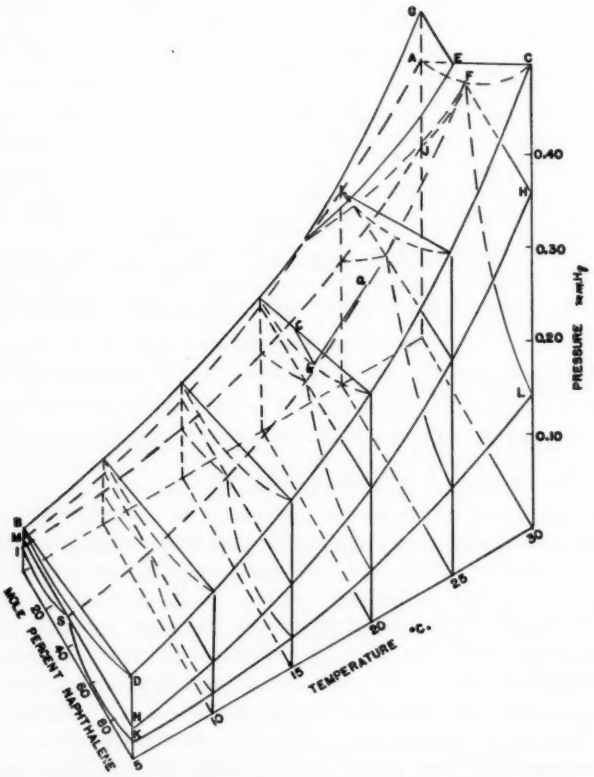

FIG. 2. A perspective drawing of a portion of the *P/T/c* space-model for the system *o*-nitrophenol–naphthalene.

solids as a function of temperature. The surface *GMNH* is a ruled surface generated by an infinite collection of isobaric, isothermal tie lines. The mole ratio of the two components in the vapor phase above solid mixtures at any temperature is equal to the ratio of the vapor pressures of the pure solids at that temperature, if the vapors are assumed ideal. Variation of vapor composition with temperature is given by the curve *FS*.

Because no vapor pressure data for solid *o*-nitrophenol could be found in the literature and because the existing vapor pressure data for solid naphthalene were not altogether consistent, vapor pressure values for the solid components were calculated from a knowledge of liquid vapor pressures. Liquid vapor pressures were obtained from Stull's compilation (5). The heat of vaporization of each pure liquid was calculated from a conventional log p vs. $1/T$ plot. Heats of fusion of the two solids were available in the literature (1). The sum of the heat of vaporization and the heat of fusion for each component at its triple point was taken as the heat of sublimation for that component. By extrapolating the liquid vapor pressure data to temperatures below the melting points of the respective components, a value of the vapor pressure for each supercooled liquid at the eutectic temperature was obtained. An assumption was then made that Raoult's law was obeyed by the eutectic liquid, and from this law a value for the vapor pressure was derived for each pure solid at 30°C. Substituting these vapor pressures and the previously derived heats of sublimation into the Clausius–Clapeyron equation, a vapor pressure equation for each solid component was established. The vapor pressure equations employed were: for solid *o*-nitrophenol, $\log p(\text{mm.}) = -3634/T+11.32$ (*a*) and for solid naphthalene, $\log p(\text{mm.}) = -3516/T+10.71$ (*b*).

The variation of vapor pressure with temperature for supercooled liquid naphthalene is shown in Fig. 2 by the curve *CD*. *AB* is the vapor pressure curve for supercooled liquid *o*-nitrophenol. The supercooled liquid–vapor equilibrium surface was obtained by again assuming the validity of Raoult's law for solutions of *o*-nitrophenol and naphthalene.

C. Discussion

The process by which vapors generated above solid mixtures condense to yield supercooled liquid solutions can be illustrated with reference to the space-model. If we consider a simple experiment in which a mixture of the solids *o*-nitrophenol and naphthalene is held at one temperature in a sublimation well of the sublimation apparatus and a "cold-thumb" condenser at some lower temperature, the following phenomena can occur: First of all the mixed vapor arising from the solids at the higher temperature can simply condense to give a mixture of solids. It is also possible, however, for the vapor, as it is cooled, to pass from the solid–vapor surface without condensing into solids. If this vapor is cooled to a sufficient extent, the point in space representing the variables of state of the vapor phase will strike the vaporous surface of the supercooled liquid–vapor loop and at this point a liquid can condense. With reference to Fig. 2 these steps are represented by the points *a*, *b*, and *c*. A solid mixture vaporized at the temperature of point *a* yields a vapor phase whose composition is also fixed by point *a*. (The point *a* lies on the dashed line

FS.) This vapor then cools in some fashion (pressure may decrease in this cooling process because of the existence of a temperature gradient between condenser and solids) until its representative point in space strikes the vaporous surface of the supercooled liquid–vapor loop at point *b*. At this point vapor may condense yielding a liquid condensate of composition *c*.

If such an experiment is performed where the solid mixture is held at the eutectic temperature and the condenser at a temperature only very slightly below this, then the model shows that eutectic vapor, *F*, will condense to give essentially the eutectic liquid, *E*.

The model of Fig. 2 is strictly applicable only to systems where *o*-nitrophenol and naphthalene are the sole substances present. However as the effect of external pressure on equilibrium between condensed phases is usually quite small, the exertion of an additional atmosphere of pressure on these solids would leave their vapor pressures essentially unchanged. This means that the vapor composition and total vapor pressure above a solid mixture in a system open to the atmosphere should be practically identical to the corresponding quantities in a closed system with air excluded. In all the experimental work solid mixtures were maintained at atmospheric pressure. Preliminary experiments were performed which showed that the composition of the liquid collected in the process, solids → mixed vapor → supercooled liquid solutions, was unaffected by external pressure in the range from *ca.* 1 to 760 mm.

Other preliminary experiments were conducted to test the effect of the composition of the solid mixtures on the composition of the supercooled solutions condensed from the vapor phase. As might be expected for a system of the simple-eutectic type, a type of system characterized by complete immiscibility of the solid components, the compositions of the liquid condensates were independent of the compositions of the solid mixtures from which they were ultimately derived.

Studies on the effect of the temperature variable consisted in thermostating the condensers of the sublimation apparatus at a particular set of temperatures and then determining, to within a few tenths of a degree, the temperatures to which solid mixtures had to be heated in order for the first liquid sublimate to form on the condensers. A period of a few hours was allowed at each temperature before a higher temperature was tried. The results of these studies are tabulated in Table I.

TABLE I

LIQUID SUBLIMATE FORMATION AS A FUNCTION OF TEMPERATURE IN THE SYSTEM *o*-NITROPHENOL–NAPHTHALENE

Temperature of solid mixture, °C.	Temperature of condenser, °C.	Composition of the liquid sublimate, mole % *o*-np
29.0	28.4	71.0
28.5	27.5	71.0
27.0	25.5	71.0
25.5	23.5	71.5
24.0	21.5	72.5
23.0	19.5	73

Eutectic composition for this system: 71.0 mole % o-nitrophenol. Precision of the analyses: 0.5–1 mole % o-nitrophenol.

The first feature that can be brought out from Table I is arrived at by comparing the first and second columns in that table. It is seen that at the higher solid temperatures only small temperature differences had to be maintained between the sublimation wells and condensers in order for liquid sublimate to form. At lower temperatures the required temperature differences became progressively greater. These temperature differences, considered as a function of temperature, indicate the manner in which the two surfaces, solid–vapor and liquid–vapor, are oriented with respect to each other in the composition region along the dashed line *FS* of Fig. 2.

The variation of the composition of liquid sublimate with the temperatures of generation and condensation of mixed vapors is seen in the third column of Table I. It is noted that at higher temperatures eutectic liquid was formed and that at lower temperatures a trend was established in the direction of somewhat higher concentrations of *o*-nitrophenol in the liquid sublimate. Though the difference in composition of the liquid at the highest and lowest temperatures was slight, it was still felt to be outside the range of experimental error.

Calculations stemming from equations (*a*) and (*b*) indicate that at the eutectic temperature the composition of the vapor in equilibrium with solid *o*-nitrophenol and naphthalene should be about 60 M.% *o*-nitrophenol and should increase to about 62–63 M.% *o*-nitrophenol at temperatures of 5° or 10°C. Constant-temperature cross-sections of the space-model for the temperature range from 30° to 10°C. were constructed and from these cross-sections the compositions of the liquid in equilibrium with a vapor containing 60 M.% *o*-nitrophenol were estimated. For example, the estimated liquid composition at 30°C. was 71 M.% *o*-nitrophenol; at 10°C., 74 M.% *o*-nitrophenol.

From these considerations we can see that even if vapor composition in this system did not change with temperature, we should expect a slight change in liquid composition, increasing percentages of *o*-nitrophenol in the liquid at the lower temperatures. Add to this effect the possibility of a slight enrichment of the vapor phase in *o*-nitrophenol content at lower temperatures and it is all the more to be expected that some change in liquid composition should occur with decreasing temperature of liquid formation.

MICROSCOPIC STUDIES

In order to investigate a large number of systems and thus to prove the general nature of the phenomenon, solids → mixed vapor → supercooled liquid solution, rapid semiquantitative microscopic methods were employed. The microscopic studies served to show that supercooled liquids could be condensed from the vapor phase in a number of systems of the unary, binary, ternary, and quaternary types.

In the microscopic sublimation studies mixtures containing approximately equal weights of all the components of a system of a given type were first prepared. Samples of these mixtures were placed on a 12-mm. cover glass maintained at one level in the sublimation chamber insert of the microscopic hot-stage. At a level about 3 to 4 mm. above the solids a 25-mm. cover glass was supported. The stage was heated at a rate of 0.2°C. per minute and the

lower surface of the upper cover glass was observed microscopically during the heating process. The lowest temperature at which a microscopically visible liquid deposit appeared was recorded; this temperature was called the liquid sublimation temperature. Also for each system a number of experiments were performed in which the solid components at the lower level were maintained out of physical contact. In some cases, after a liquid sublimate had started to form, the temperature of the stage was maintained at a constant value for a period of time and larger quantities of supercooled liquids were thereby collected. These liquids were crystallized at dry ice temperatures and the resulting crystallized samples observed upon reheating.

DISCUSSION

Representative data obtained in these microscopic studies are compiled in Table II. A number of interesting observations can be drawn from these data. It is noted first of all that in every case liquid was obtained at tempera-

TABLE II

MICROSCOPIC DATA FOR THE FORMATION OF LIQUID SUBLIMATES

System type	System	Melting point, °C.	Eutectic temperature	Liquid sublimation temperature,* °C.
Unary	Acenaphthene	93.6	—	>60
	Azobenzene	67.4	—	51.2
	Benzil	95.0	—	>60
	Naphthalene	80.0	—	57.9
	α-Nitronaphthalene	56.9	—	44.3
	o-Nitrophenol	44.9	—	36.4
	p-Nitrophenol	113	—	>60
Binary	o-Nitrophenol Naphthalene	44.9 80.0	30.0	27.8[a]
	Azobenzene Naphthalene	67.4 80.0	41.8	35.0[b]
	α-Nitronaphthalene Naphthalene	56.9 80.0	35.1	29.8[c]
	α-Nitronaphthalene Azobenzene	56.9 67.4	35.8	30.9
	o-Nitrophenol Azobenzene	44.9 67.4	28.7	28.3
	Azobenzene Acenaphthene	67.4 93.6	48.6	38.5[d]
	Acenaphthene Benzil	93.6 95.0	63.9	57.3[e]
	Azobenzene Benzil	67.4 95.0	52.5	41.6[f]
	Azobenzene p-Nitrophenol	67.4 113	49	48.5

TABLE II (*concluded*)

System type	System	Melting point, °C.	Eutectic temperature	Liquid sublimation temperature,* °C.
Ternary	*o*-Nitrophenol Azobenzene Naphthalene	44.9 67.4 80.0	18.6	16.2[g]
	α-Nitronaphthalene Azobenzene Naphthalene	56.9 67.4 80.0	21.6	19.6[h]
	Azobenzene Acenaphthene Benzil	67.4 93.6 95.0	37.8	35.5[i]
	Acenaphthene Benzil *p*-Nitrophenol	93.6 95.0 113	50	46.5
	Azobenzene Acenaphthene *p*-Nitrophenol	67.4 93.6 113	44.4	38.0
	Azobenzene Benzil *p*-Nitrophenol	67.4 95.0 113	40.0	38.5
Quaternary	Azobenzene Acenaphthene Benzil *p*-Nitrophenol	67.4 93.6 95.0 113	32.0	30.5

Notes on the melting points of crystallized sublimates:
(a) Beginning melting point, 29.8°C., end melting point, 29.8°C.; (b) 42.0, 43.5; (c) 34.5, 35.5; (d) 47.3, 51; (e) 63, ca. 67; (f) 51, 53.5; (g) 17.5, 19.5; (h) crystallization incomplete, 24; (i) 37.4, 41.5.

**The temperature of the surroundings of the microscope stage was maintained at about 10° to 15°C. below the eutectic temperature for each sublimation study.*

tures below the lowest eutectic temperature. This observation was made both in the case of mixtures and for the "non-contact" studies. Except for small differences in liquid sublimation temperatures the phenomenon of condensation of supercooled liquid solutions above solids did not depend upon whether the solids were in physical contact.

The fact that in every case liquid formation in a binary system took place at a lower temperature than in either unary indicates that both components were present in the supercooled liquid in the binary system, since at these temperatures the vapor phase could not have been saturated with respect to either of the pure components. A similar situation existed in the ternary and quaternary systems.

In a number of experiments (see footnotes to Table II) a sufficient amount of liquid was collected to allow for a subsequent melting point determination on a crystallized sample. The fact that all preparations began to melt at or near the appropriate eutectic temperatures shows that each liquid sublimate

must have contained all the components present in the original solid samples. (It is noted that in a few instances the "beginning melting point" for a recrystallized sample was somewhat below the indicated eutectic temperature. Here it is probable that crystallization was incomplete at dry ice temperatures. The "beginning melting point" simply signifies the temperature at which a solid phase began to disappear rapidly.)

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HYDROGEN OVERPOTENTIAL ON ALUMINUM[1]

By D. J. Hansen[2] and F. E. W. Wetmore

ABSTRACT

The hydrogen overpotential of pure and impure aluminum in 0.1 N H_2SO_4 at 25° has been studied. The effect of the autocorrosion of the metal has been interpreted and the role of impurities in determining the overpotential and the rest potential has been shown. As well, the build-up and decay of the overpotential has been studied; the behavior is much more complicated than that of noble metals.

Studies of hydrogen overpotential on aluminum have been few (2, 3, 5, 6, 7, 8) and in most cases details of procedure and the degree of purity of the metal are lacking or there is indication that proper experimental precautions (1) have not been taken. In no case was the rate of corrosion reported, although it may have been substantial. The investigation reported here was an exploration at low current densities, for which there are no serious doubts about the homogeneity of current density distribution.

EXPERIMENTAL

The electrolyte used for all experiments was 0.1 N H_2SO_4, a concentration selected as a compromise between the desires for high conductivity and low rate of corrosion. The water was of "conductivity" grade, $k = 8 \times 10^{-7}$ ohm^{-1} $cm.^{-1}$, the acid redistilled reagent quality. The electrolyte was purged with purified hydrogen and subjected to lengthy pre-electrolysis, according to the method recommended by Bockris and co-workers (1).

The aluminum cathode and platinum anode of the cell were in separate compartments connected through closed ungreased stopcocks wet with solution. Hydrogen was bubbled continuously about both electrodes. An auxiliary cathode of platinum was available for pre-electrolysis. A capillary probe near the cathode surface led to a reference electrode, 0.1 N H_2SO_4/Hg_2SO_4, Hg. Four types of cathode material were selected for study: (I) rolled sheet, 99.995% pure, (II) cast polycrystalline, 99.995% pure, (III) single crystal, 99.995% pure, and (IV) "commercially pure" ingot, 99.5% pure. The cathodes were electropolished in a perchloric acid bath, then mounted in a Teflon box which exposed only one flat face. Unless stated otherwise, current densities mentioned refer to the apparent area of this face.

The currents used were electronically regulated. The potential difference between the probe and cathode was passed to a direct-coupled amplifier of very high impedance (about 10^{13} ohms) and thence to a torsion string galvanometer (Model TSB-A29, Kipp en Zonen, Delft). The deflection of the galvanometer could be recorded on film in a drum camera. Alternatively, a potentiometer was used for steady state readings. Rates of corrosion were determined by measurement of the weight loss of the sample; a resistance–capacitance bridge

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Contribution from the Electrochemical Laboratory, University of Toronto, Toronto 5, Canada.
[2]*Present address: Metals Research Laboratory, Box 580, Niagara Falls, N.Y., U.S.A.*

was used to show that the resistance, and hence the thickness, of the oxide film did not change sufficiently to cause appreciable error in the weight loss measurements.

RESULTS AND DISCUSSION

In the following description the overpotential will be defined as the potential of the reversible hydrogen electrode in the electrolyte less the potential of the cathode, and will therefore be positive.

Figure 1A shows the overpotential plotted against the logarithm of the applied current density, i_z, for sample I; the curves for samples II and III

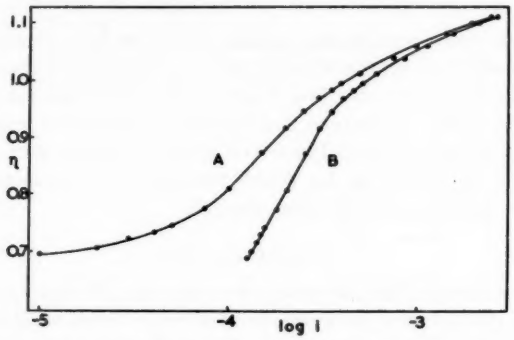

FIG. 1. Overpotential of sample I as a function of the applied current density (A) and the total current density (B).

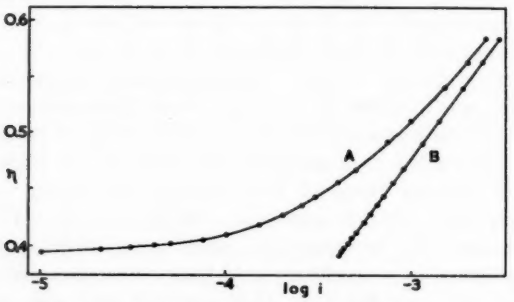

FIG. 2. Overpotential of sample IV as a function of the applied current density (A) and the total current density (B).

are similar. Figure 2A shows the curve for sample IV; it differs from the others in not exhibiting a bend to lower slope at the higher current densities. All of these curves show a distinct deviation from the linearity frequently found for unreactive metals, expressed by Tafel's relation

$$\eta = b \ln(i/i_0). \qquad [1]$$

Even when there is no applied current there is a cathodic current due to the autocorrosion of the sample. Under this condition the cathodic current I is

identical with the corrosion current I_a. With application of an electrolyzing current I_x, the total cathodic current I equals I_a+I_x. Table I gives corrosion

TABLE I

CORROSION CURRENT DENSITIES AND REST POTENTIALS

Sample	I	II	II*	III	IV
i_a, μa.cm.$^{-2}$	25	28	22	33	103
E_r	0.675	0.650	0.640	0.625	0.368

Second series, one month after first.

current densities from weight loss determinations through Faraday's law. These data were obtained without applied current. Weight loss measurements made with electrolyzing current flowing showed that the corrosion current is enhanced by current densities above some 75 μa. cm.$^{-2}$. These corrosion rates were not as reproducible as those taken without electrolyzing current. Fortunately this is not a serious concern in determining $\log(i_a+i_x)$. For typical example, at $i_x = 267$ with $i_a = 50$, a deviation of 10 in i_a would represent only 0.015 in $\log(i_a+i_x)$. The curves B of Figs. 1 and 2 are plotted with $\log(i_a+i_x)$ as the abscissae. These curves show that at the lower current densities the overpotential is indeed linear in the logarithm of the *total* cathodic current density.

It was found that the rest potentials of the samples (E_r at $I_x = 0$) were diverse and were decreased after prolonged electrolysis. There exists, however, a relationship between the corrosion current density and the rest potential. This is shown in Table I; the rest potentials recorded were taken before prolonged electrolysis.

With the exception of sample IV, the cathodes showed a decrease in the slope of the "Tafel curve" at the higher current densities. Such a change in slope is sometimes attributed to a change in the mechanism of the discharge process. In this case an explanation of more direct appeal is to attribute the change to an alteration in the nature of the active cathodes. It will be assumed that both the aluminum and the traces of impurities present can act as cathodes. The total cathodic current I can then be visualized as consisting of two terms, I_1 for that part of the current accepted by the aluminum, and I_2 for that accommodated by the impurities. Thus

$$I_a+I_x = I_1+I_2. \qquad [2]$$

Spectroscopic analysis showed iron and copper to be the major part of the 0.005% of impurity present in samples I, II, and III. From earlier work (3) iron and copper are known to have low overpotentials at low current densities with marked rise at very high current densities. It is possible that these impurities can accommodate the greater part of the current at low current densities, even though their exposed areas are extremely minute, since the overpotential of the aluminum at very low current density may be greater than the overpotential of the impurities at the relatively high current densities

corresponding to their small exposed areas. This, and the variation in the slope of curve B of Fig. 1, can be explained more formally in terms of the behavior of mixed cathodes.

Let b_1 denote the slope of the curve of overpotential of aluminum plotted against ln I_1. Then $b_1 = I_1(d\eta/dI_1)$. Similarly for the impurities, $b_2 = I_2(d\eta/dI_2)$. Further, let b^* denote the slope of the curve for the mixed cathodes (the actual experimental curve). Then $b^* = (I_1+I_2)[d\eta/d(I_1+I_2)]$. It follows that

$$[3] \qquad 1/b^* = I_1/b_1(I_1+I_2)+I_2/b_2(I_1+I_2) = \phi_1/b_1+\phi_2/b_2,$$

in which ϕ_1 is the fraction of the total cathodic current flowing to the aluminum and ϕ_2 that to the impurities. Thus it is seen that b^* becomes identical with b_1 only as ϕ_1 becomes much greater than ϕ_2. From the form of the curves B of Figs. 1 and 2, the impurities appear to be the predominant cathodes at the low current densities and b^* can be expected to approach b_1 only for high current density on very pure metal. Some confirmation of this viewpoint can be obtained from examination of the rest potentials of the samples (Table I). Sample IV contains one hundred times as much impurity as the other three; the ratio of the exposed areas of impurities will be about the same number. The current density of autocorrosion is therefore much less on the impurities of sample IV than on those of the other three; this is reflected in the much lower rest potential of sample IV. It is consistent with this observation to say that the rest potential is simply the overpotential on the impurities at the particular current density defined by the corrosion current and the area of the impurities exposed. This concept is supported by calculation of the value of the quotient: the difference between the rest potential of sample IV and that of another sample, divided by the natural logarithm of their current density ratio (taking into account the 100:1 ratio of areas of impurities). From Table I the values of the quotients range from 0.074 to 0.100, in agreement with those for iron and copper, but much too high for aluminum.

It is now clear why the rest potential varies without apparent change of conditions, why it varies with the proportion and kind of impurity, why it is affected by prolonged electrolysis, and why the overpotential decreases slightly with prolonged electrolysis. The rest potential is very sensitive to the area of impurites exposed, which can vary as aluminum is dissolved away. Even minute traces of ions of more noble metals present in the electrolyte, whether initially or by dissolution, can change the effective area of active cathode by plating out as the sample is driven cathodically. This emphasizes the need for high purity in both the aluminum and the electrolyte.

Although definite values for the parameters of the overpotential of aluminum cannot be stated from this work, it is evident that both b and i_0 of equation [1] must have very small values, even smaller than those previously reported. The determination of precise values will require the use of extremely pure metal at current densities as high as can be consistent with homogeneous distribution of the current. Work with zone-crystallized metal is proposed.

Both build-up and decay of overpotential as functions of time were determined with the galvanometer and drum camera. For noble metals the initial and greater part of the potential-coulomb curve of build-up is linear; with aluminum cathodes the curve is not linear in any part, in agreement with the following considerations. The generally accepted theory of overpotential leads to an expression for the rise of potential with time of the form (4)

[4] $$dE/dt = I/C - K.\exp(E/b),$$

in which C is a constant with the dimensions of capacitance, K is a constant, and b is the slope of the "Tafel curve" (equation [1]). Before an electrolyzing current is applied there exists the steady state of rest potential, E_r, and the corrosion current, I_a. Equation [4] then becomes

[5] $$0 = dE/dt = I_a/C - K.\exp(E_r/b).$$

With application of an electrolyzing current, I_z, equation [4] becomes

[6] $$dE/dt = (I_a + I_z)/C - K.\exp(E/b).$$

The initial slope of the build-up curve is given by equation [6] with equation [5] valid at $t = 0$:

[7] $$(dE/dt)_{t=0} = (I_a + I_z)/C - K.\exp(E_r/b) = I_z/C.$$

For noble metals the value of E_r is small and the exponential term remains small over a considerable portion of the build-up. With aluminum the condition is quite different. The rest potential represented from 50 to 85% of the ultimate overpotential in the range of conditions used here. Therefore the exponential term was appreciable at all stages of the build-up and not even the initial part of the build-up curve was linear. The initial slope was determined by extrapolation to zero time of the secants from the rest potential to the first several points on the build-up curve. Table II gives the data for cathode III, for example.

TABLE II

C FROM SLOPES OF BUILD-UP CURVES

i_z, μa.cm.$^{-2}$	55	91	127	215	273	364	545	727
C, μf.cm.$^{-2}$	28	25	26	26	22	22	24	17

Potential decay curves also showed complication not found with noble metal. The curves were not superimposable by a simple time shift, θ, as found for silver (4), but a value of Δt could be found such that E was linear in $\log(t+\Delta t)$ over the first 90% of the decay curve. With the assumption that Δt corresponds to θ, C was calculated as $(I_a+I_z).\Delta t/k$; the value of k was determined from the slope of the curve of E against $\ln(t+\Delta t)$. Values of C were also calculated by a method similar to that used for the build-up curves. After a build-up of potential there exists a steady state of overpotential and a steady state of cathodic current. Equation [4] then takes the form

[8] $$0 = dE/dt = (I_a + I_z)/C - K.\exp(\eta/b).$$

When the electrolyzing current is removed, $I_z = 0$ and equation [4] takes the form appropriate to decay

$$[9] \qquad (dE/dt)_{t=0} = I_a/C - K.\exp(\eta/b) = -I_z/C.$$

Table III shows values of C calculated by the two methods, for sample III.

TABLE III

QUANTITIES DETERMINED FROM DECAY MEASUREMENTS

i_z, μa.cm.$^{-2}$	91	127	215	364	727
$-dE/d[\log(t+\Delta t)] = k$	0.195	0.262	0.257	0.204	0.194
C, μf.cm.$^{-2}$, eq. [9]	22	17	24	20	20
$C = (i_a+i_z).\Delta t/k$	32	32	31	19	16

ACKNOWLEDGMENTS

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SKELETAL SILVER CATALYSTS FOR THE OXIDATION OF ETHYLENE TO ETHYLENE OXIDE[1]

By A. Cambron[2] and W. A. Alexander

ABSTRACT

Skeletal silver catalysts of high specific activity have been prepared by the removal of calcium from calcium–silver alloys. The activity of these catalysts in the oxidation of ethylene to ethylene oxide has been investigated. Catalysts prepared by the removal of the other alkaline earth metals from their alloys with silver have also been studied. It has been found that catalysts prepared from calcium–silver alloys show a higher specific activity and are more stable and more conveniently prepared than the catalysts from the other silver alloys investigated.

INTRODUCTION

The increasing interest in ethylene oxide as a starting material in organic syntheses is shown by the numerous references in the recent current and patent literature not only to improved methods of producing this versatile chemical, but also to its use in the preparation of other aliphatic chemicals and derivatives. A survey of the literature was included in a recent communication (7).

Considerably more work has been done on the direct oxidation of ethylene to ethylene oxide than on the older chlorohydrin method since the specific activity of silver as a catalyst in that reaction was first reported by Francon (4). The reason for this is that the direct catalytic oxidation offers a more attractive method provided the complete oxidation of ethylene, which is also promoted by the silver catalyst, is limited.

Metallic silver is the only substance which has been found to have a specific catalytic effect on the oxidation of ethylene to ethylene oxide. The methods described in the literature for the preparation of silver catalysts have been almost exclusively by the precipitation of the finely divided metal or of the oxide, from solutions of a silver salt or by the thermal decomposition of a silver salt. The use of numerous oxides or metals as promoters has also been mentioned in the literature (8, 11, 13), but in all cases the oxides are added as a distinct solid phase, or the added metal remains in the catalyst.

The preparation of an active catalyst by the thermal decomposition of silver oxalate in the presence of water under pressure was described in a previous paper (7). It was found that the activity of the latter catalyst could be increased by the use of lime and stannous oxide as promoters. The pronounced action of calcium oxide as a promoter even when present in very small amounts suggested that a reduction of the calcium oxide by silver might take place locally on the surface of the catalyst, resulting in alteration in the surface of the catalyst by the momentary formation of a calcium silver compound, followed by the regeneration of calcium oxide and of metallic silver by the action of the oxygen in the reacting gases. Dowden (3) in a recent paper has

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[2]*Deceased February, 1952.*

pointed out the possibility that irreducible oxides in the presence of a reducing metal such as copper, and one would expect silver to behave similarly, may lead to the formation of a metallic surface phase. Even if this only resulted in the formation of a chemisorbed layer of the added metal, it would be expected to have a strong influence on the activity of the surface.

In the previous work on the use of calcium oxide as a silver catalyst promoter, it was observed that this oxide, in addition to promoting the oxidation of ethylene to ethylene oxide, also strongly promoted the complete oxidation of ethylene to carbon dioxide and water. In order to study the effect of calcium on the catalyst surface in the absence of calcium oxide a calcium–silver alloy was prepared and the activity of the surface was determined after removing the calcium metal with a suitable reagent. In this manner a very active and very stable skeletal silver catalyst was obtained which possessed an appreciably higher selectivity than finely divided silver catalysts prepared by known methods.

EXPERIMENTAL

In order to determine the effect of the removal of the calcium component of the alloy on the structure of the remaining silver skeleton, an X-ray examination of the alloy was made. This gave a spectrum different from that of silver owing to the presence of the calcium–silver compound and of a eutectic. After removal of the calcium the characteristic silver lines corresponding to the face-centered cubic arrangement of crystalline silver reappear and the sharpness of these lines indicates that the silver crystal units must form particles of the order of 1000 Å in size.

The first calcium–silver alloys were prepared with a calcium content of 5–7%. It was found, however, that complete removal of the calcium required prolonged treatment of the alloy with steam after grinding to 20–30 mesh. Alloys were therefore prepared with a higher calcium content, in the range 7–12% calcium. These are considerably more brittle and could be ground conveniently to the required size for complete removal of the calcium. It is interesting to note that the calcium–silver alloys themselves possess no specific activity in the oxidation of ethylene and that maximum specific activity is obtained by as complete a removal as possible of the calcium.

In the course of the work done on the preparation of skeletal silver catalysts from silver alloys a number of other alloying elements from groups one to four have been studied, namely lithium, magnesium, strontium, barium, zinc, aluminum, lanthanum, cerium, and tin. Although a few of these alloys showed some activity after complete or partial removal of the alloying elements, with the possible exception of barium none showed as high a specific activity as the catalysts prepared from calcium–silver alloys. This may in part be due to the fact that the removal of calcium from the calcium–silver alloy can be done more readily and under less drastic conditions than is the case with the other metals.

Preparation of Silver–Calcium Alloys

The calcium–silver alloys were prepared by melting the required amount of silver in a crucible made from a stainless steel or iron tube, fitted with a

¼ in. iron thermocouple tube which also served as a hand stirrer and was so arranged that an argon atmosphere would be maintained in the crucible. A slight excess of freshly cleaned calcium metal was then added to the molten silver. After the molten mass was kept above the melting point of the alloy for about one minute with stirring, the alloy was allowed to cool, or was quenched, and the solid ingot obtained was recovered by stripping off the metal tube. By a later procedure, especially with large melts, the silver was first allowed to solidify and then dissolved slowly by alloying with the calcium at 750° to 850°C., to decrease the rate of gas evolution and to eliminate the danger of a mild explosion.

Silver alloys of other alkali and alkaline earth metals were prepared by the same procedure.

Activation of Silver Catalysts

Several methods were tried for removing the added metal from the silver alloys. Simple refluxing in acetic acid with or without diluted oxidizing agents such as hydrogen peroxide or potassium permanganate did not produce a highly active catalyst. Since the present work was concerned mainly with alloys of silver with metals of groups II and III, many of which react with steam at temperatures below 350°C., the usual initial step in the activation procedure was the treatment of the alloys, ground to about 20–30 mesh, with steam at 300–450°C. for about six to eight hours, or with water in an autoclave at 200–250°C. for about four hours. Control of temperature in the activation treatments is necessary and is aided by use of only small amounts of powder in one place to prevent accumulation of heat of reaction. With silver alloys containing magnesium, strontium, and barium, it was found difficult if not impossible to react the added element completely. Tests carried out with other than calcium alloys were therefore qualitative in character, but did indicate that the calcium alloy was the most convenient to use.

Variations in the activation procedure which were successful included the heating of the alloy in a moist air stream or in the off-gas from a reactor for long periods at about 400°C. followed by leaching with warm acetic acid. Refluxing in acetic acid with repeated additions of 5% hydrogen peroxide, treatment with 15% nitric acid, and variations of the autoclaving such as addition of alcohol, hydrogen peroxide, dioxane, phenol, borax, and ethylene glycol to the water resulted in only normally active catalysts.

After conversion of the added element to the hydroxide by steam, the latter was leached out by refluxing with 20% acetic acid for one hour followed by washing the residue with distilled water and sometimes alcohol. Formic and citric acids may also be used to dissolve the calcium hydroxide.

Apparatus and Materials

The test apparatus arrangement was similar to that described before (7) except that the ethylene was taken directly from the cylinder and the reaction tubes now consisted of ½ in. diameter holes in an aluminum block. The bottom of each reaction hole was closed by a bed of coarse silver granules which served as a preheater for the reactants. Most alloys were crushed to 20–35 mesh,

and weighed lots placed on top. The temperature was measured by a chromel alumel thermocouple with a silver strip about $\frac{1}{4}$ in. $\times$ 1 in. $\times$ 0.020 in. brazed to the junction, which was covered by the catalyst. The products were normally vented to a water tower and the solution discarded, or passed to the analytical part of the apparatus. No change was made in the analytical procedures.

Ethylene of U.S.P. grade was obtained from the Ohio Chemical Co. and produced by the dehydration of alcohol. It was used without further purification. The air supply was passed through an activated charcoal bed and, in later tests, through a tube containing heated silver catalyst as well. Both reactant streams were measured by calibrated flowmeters. The silver was mint grade granules and the calcium, magnesium, strontium, and barium probably distilled products of the Dominion Magnesium Company.

Some attempts were made to modify the disposition of the catalyst bed, for better temperature control on a larger scale. Pressing of the silver granules into pellets using various pressures showed that the activated catalyst could not be deformed without loss of activity. However, further tests with alloys having some plasticity showed that active catalysts could be prepared from pellets or disks of alloy granules. Mixing the alloy granules with other metal powders to improve the bonding showed that aluminum, brass, iron, and monel decreased the activity severely, while pure silver was neutral.

RESULTS

As mentioned above, calcium–silver alloys produced the most stable catalysts with the highest activity. Usually catalysts from these alloys exhibited an increase in activity, as measured by selectivity, to a maximum at about 10–20 days with a subsequent slow decrease. This decline was normally very

TABLE I

STABILITY OF CALCIUM–SILVER CATALYST

Composition: initial: Ca 9.25%, Ag balance; activated: Ca 0.6%, Ag balance; ethylene: 2.0 l./hr.; air 30 l./hr.; catalyst weight: 17 gm.; mesh: −20+35; volume: 7.9 cc.

	Temperature		Conversion %'s		
Day	Catalyst	Block	C_2H_4O	Total	Selectivity
1	285	259	39.3	96.0	41.0
9	277	259	42.0	81.5	51.5
33	270	260	41.5	76.0	55.0
43	287	275	45.0	87.5	51.5
71	260	260	35.3	66.1	53.5
111	266	261	40.6	75.0	54.1
149	272	263	39.6	81.7	48.5
195	262	260	18.7	27.6	67.8
201	266	261	42.3	74.0	57.2
232	286	278	46.6	88.8	51.4
261	266	264	21.8	37.0	57.0
291	269	263	40.3	75.1	53.7
327	266	260	35.3	72.1	49.1
344	263	260	35.1	68.1	51.4
350	—	260	15.2	23.0	66.1
365	263	260	32.3	60.5	53.4

slow as numerous tests were carried on for periods of up to about 12 months, with a high level of activity at the end of the test. One such experiment is summarized in Table I. This catalyst was activated by treating with steam for one-half hour, at 150°C. initially and gradually raising the temperature to 350°C., followed by one hour at 340–355°C. The lime was removed by 20% acetic acid followed by water and methanol washings. This test was carried on for more than a year, the catalyst being poisoned by unknown substances three times with subsequent recovery to normal activity levels. Results with a number of calcium–silver alloy catalysts are shown in Table II. Activation of

TABLE II

ACTIVITIES OF CATALYSTS FROM CALCIUM–SILVER ALLOYS
Ethylene: 2 l./hr.; air: 30 l./hr.; block temperature: 260°C.

Composition, %Ca			Duration of test, days	Catalyst temperature, °C.	Typical conversion %'s			Catalyst	
Initial	Final	Day			C_2H_4O	Total	Selectivity	Wt., gm.	Mesh
9.5	1.25	37	78	263	42	66	64	20	20–35
10.3	4.3	10	37	268	36	67	53	16	20–35
9.9	1.4	26	37	272	46	87	53	16	20–35
8.2	0.3	27	60	274	43	83	52	16	20–35
6.5	1.8	9	25	270	32	64	51	16	20–35
9.6	0.2	44	161	274	46	76	60	16	10–20
10.3	0.0	60	111	272	47	86	55	16	20–35

these alloys was by heating in a current of steam at 300° to 400°C., followed by leaching with acetic acid and with water. As complete removal of calcium as possible from an 8 to 11% alloy is the preferred procedure, since a high residual calcium content apparently decreases the stability of the catalyst.

Catalysts prepared from magnesium and strontium alloys showed a lower selectivity at comparable total reaction levels than calcium–silver. Barium apparently approached the activity of calcium, but for economic reasons and because of its reactivity it was not extensively tested. Results obtained with these alloys are shown in Table III, from which it will be noted that the yields are considerably lower than with the calcium alloys of Table II.

TABLE III

ACTIVITIES OF SILVER CATALYSTS FROM MAGNESIUM, STRONTIUM, AND BARIUM ALLOYS
Ethylene: 2 l./hr.; air: 30 l./hr.

Composition, %		Temperatures, °C.		Typical conversions, %			Gm. of catalyst	
Initial	Final	Block	Catalyst	C_2H_4O	Total	Selectivity		Activation procedure
Mg 5	3	6.4	213	375	16	82	19	11.5	Steam at 375°, leach with acetic acid
Mg 17	13		260	264	12	28	43	16	Steam at 375°, leach with acetic acid
Sr 5	—		200	222	12	32	39	—	Moist air at 400° for 45 hr., leach with acetic acid
Ba 5	—		270	273	4	11	35	—	Moist air at 400° for 45 hr., leach with acetic acid
Ba 21	3		259	264	35	91	38	16	Steam at 375°C., leach with acetic acid
Ba (3)		0.2	249	276	37	85	43	15.6	Reactivated above catalyst by above procedure

TABLE IV

ACTIVITIES OF CATALYSTS FROM CALCIUM–MAGNESIUM–SILVER ALLOYS
Ethylene: 2 l./hr.; air: 30 l./hr.; catalyst size: −20+35 mesh

Composition, %		Temperatures, °C.		Typical conversion, %				
Initial	Final	Block	Catalyst	C_2H_4O	Total	Selectivity	Day	Gm. of catalyst
Mg 19.8 Ca 4.3	10.7 0.0	250	278	26	83	31	16	16
Mg 10.3 Ca 4.8	0.0 0.0	259	273	27	94	28	9	16
Mg 5.4 Ca 5.8	0.0 0.2	265	274	16	48	34	2	15.3
Mg 5.0 Ca 9.3	0.0 0.2	260	272	46	98	47	13	16
Mg 2.5 Ca 11.6	0.0 0.4	259	271	43	98	44	11	16

Experiments with the ternary magnesium–calcium–silver alloys are summarized in Table IV. These were activated by steaming at 350° to 375°C. and leaching with acetic acid followed by washing with water and drying. As mentioned earlier, the removal of a large excess of magnesium is difficult, and the yields or selectivities of the resulting catalysts tend to be considerably lower than with calcium–silver alloys. Catalysts prepared from alloys with an excess of calcium apparently show activities similar to the binary calcium–silver alloys.

Several metals from groups I to IV of the periodic table were tried as substitutes for calcium. In some cases the added element could not be removed readily while in others the residual silver showed no enhanced catalytic effect. The possible exceptions are tin and lanthanum, which were, however, inferior to the alkaline earth metals. Other elements tested were sodium, lithium, mercury, and aluminum.

The effects of many promoters, of preconditioning procedures, and of anticatalysts were also investigated. As promoters, many metals were added in minor amounts, some being partially removed during the activation procedure. In no case was any reproducible increase in yield of ethylene oxide observed. The metals tested were copper, manganese, platinum, nickel, zinc, cadmium, mercury, tin, cerium, lanthanum, as well as calcium oxide and calcium carbonate.

As will be noted in Table I the selectivity of the catalyst is usually low for the first 10 to 20 days. This induction period may be reduced to as little as two to three days by heating at the reaction temperature for about one week in an atmosphere of carbon dioxide, oxygen, steam, air, ethylene, and probably other gases. The catalyst then shows normal reactivity in other respects.

The efficiency of halogen compounds (1, 2, 5, 6, 14) and halides (12, 19) as anticatalysts in the suppression of the reaction to carbon dioxide and water has been mentioned frequently in the literature. The use of organic halogen

compounds has also been suggested in the reactivation of a poisoned catalyst or in the regeneration of an old one with low activity (20). McKim and Cambron (7) found no anticatalytic activity with an organic halogen, but a definite poisoning. The effect of inorganic halide solutions was investigated in the course of the present experiments. In only three instances were moderate increases in activity observed which might be attributed to the sodium chloride and to the hydrogen chloride treatments, the latter apparently being the more effective. Large amounts of halides acted as poisons. There was, however, some indication that this treatment would decrease the induction period in the same way as preheating. The halides tested were hydrogen chloride, potassium chloride, sodium chloride, sodium fluoride, magnesium chloride, and magnesium fluoride. Silver chromate in large amounts also acted as a poison.

On adding ethane to the feed gas, a decrease in selectivity was again observed (7). In seven experiments, 10% ethane was mixed with the ethylene and in only one was an increase in yield observed, amounting to only about 3%. In the remainder decreases of up to about 15% occurred. An additional test with 5% ethane showed a decrease of about 20%. The presence of ethane in these amounts might thus be considered undesirable.

Several papers (9, 10, 15, 16, 17, 18) have discussed the kinetics and reaction mechanisms and nothing can be added from this work. Various engineering developments in the use of these catalysts have been made in these laboratories, such as the means of disposal of the catalyst in the reactant stream to maintain close temperature control and achieve optimum reactivity. These will undoubtedly be discussed in future publications.

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THE SYSTEM LiCl–NaCl–KCl–H_2O AT 25° C.[1]

By A. N. Campbell and E. M. Kartzmark

ABSTRACT

Of the component ternary systems of the quaternary system LiCl–NaCl–KCl–H_2O, the system LiCl–KCl–H_2O has not previously been investigated. This has now been done and it is shown to be very similar to the system LiCl–NaCl–H_2O investigated by Smits, Elgersma, and Hardenberg (4). In both systems, the strongly hydrated lithium ion reduces the content of second salt to a low value at the (isothermal) invariant point.

The quaternary system of the title has been investigated, using a new method of analysis which involves the determination of total chloride and of density. The quaternary invariant composition is similar to that of the ternary invariant in the system LiCl–KCl–H_2O. In none of these systems is there formation of double salt or solid solutions and the only hydrate occurring as a solid phase is LiCl.H_2O.

The study of this system was undertaken as the first part of a comprehensive study of the five-component system containing the radicals Li_2, Na_2, K_2, Cl_2, and SO_4, and water. A similar comprehensive study on the ions of sea-water was made by van't Hoff (5) but his investigation did not extend to lithium. The present study includes, in addition to the system now described, the ternary systems (1) Li_2Cl_2–Li_2SO_4–H_2O, (2) Na_2Cl_2–Na_2SO_4–H_2O, (3) K_2Cl_2–K_2SO_4–H_2O; the quaternary system Li_2SO_4–Na_2SO_4–K_2SO_4–H_2O; and the reciprocal salt pairs (1) $Li_2Cl_2 + Na_2SO_4 = Na_2Cl_2 + Li_2SO_4$, (2) $Na_2Cl_2 + K_2SO_4 = K_2Cl_2 + Na_2SO_4$, (3) $Li_2Cl_2 + K_2SO_4 = K_2Cl_2 + Li_2SO_4$; as well as the quinquenary system mentioned above. Much of the experimental work involved has already been done but not all of it. The method of graphical representation chosen was that of Jänecke (3), the only one of reasonable simplicity. The axes of representation for Jänecke's system are the edges of a regular equal-sided triangular prism. On this model, the six vertices represent single salts and water, the edges ternary systems, the triangular surfaces quaternary systems, the rectangular surfaces reciprocal salt pairs, and the interior of the model the quinquenary system.

On reviewing the literature of the present study, we found that of the component ternary systems, viz. (1) LiCl–NaCl–H_2O, (2) LiCl–KCl–H_2O, and (3) NaCl–KCl–H_2O, system (3) was well known, and system (1) had been done by Smits, Elgersma, and Hardenberg (4); system (2) was unknown. In view of our own results for system (2) we see no reason to doubt the results of Smits, Elgersma, and Hardenberg for the analogous system (1); it appears that the highly hydrated lithium ion acts very powerfully in displacing other salts from solution, so that the isothermal invariants: LiCl.H_2O, NaCl, solution and LiCl.H_2O, KCl, solution, respectively, contain in solution very little salt other than lithium chloride. Our first task then was to carry out an investigation of the system LiCl–KCl–H_2O, at 25° C., preparatory to a study of the quaternary system named in the title.

[1]*Manuscript received January 17, 1956.*
Contribution from the Chemistry Department, University of Manitoba, Winnipeg, Manitoba.

EXPERIMENTAL

The technique of preparing and filtering saturated solutions is too well known to merit description. For the investigation of the ternary system we used Schreinmakers' method of the 'wet rest'. No such method is available for the quaternary system, neither is it necessary since the nature of all solid phases is known. The chemicals used were all either B.D.H. 'Analar' or Merck's 'reagent' grade. They were used without further purification since very slight traces of impurity are without effect on studies of this kind.

The great difficulty in studies involving mixtures of alkali cations is a method of analysis. Any chemical method would be laborious and too inaccurate for the present purpose. It is possible in theory, however, to analyze any three-component mixture by determining any two physical properties for all proportions of the three components. One of us used the method, very successfully, for the analysis of liquid mixtures of benzene – ethyl alcohol – carbon tetrachloride (2), but here the problem is simpler, since the amount of water does not enter as a fourth variable. To overcome this difficulty we proceeded in the following way: after determining total solubility in the usual manner, exactly 10 gm. of the anhydrous solid mixture was dissolved in water and diluted to exactly 100 ml. and the density and total chloride content determined. Because of the very hygroscopic nature of lithium chloride, it was not advisable to weigh exactly 10 gm. of the mixture and therefore the total weight of solid mixture was dissolved in water, the solution weighed, such an aliquot taken as corresponded to 10 gm., and this then made up to 100 ml. In their study of the system LiCl–NaCl–H_2O, Smits, Elgersma, and Hardenberg (4) used the viscosity of mixtures of constant total composition as the analytical method. When the chloride contents and densities, or rather the density minus one, of all possible mixtures of LiCl, NaCl, and KCl, are plotted on two separate triangular diagrams, and points of equal density and of equal chloride content respectively are joined by curves, the method of analysis is complete. The density of an unknown mixture places it on a curve of density and its chloride content on a curve of chloride content. Since fortunately these two curves always intersect sharply, the point of intersection represents the composition of the mixture. On previous occasions, we had adopted the method of placing one diagram exactly above the other and illuminating strongly from below. In the present instance, we found it better to plot both sets of results on one diagram, as shown in Fig. 1.

The densities were determined in a 25 ml. specific-gravity bottle. In order to obtain an accuracy of one per cent in the analysis, the density must be determined to two units in the fourth decimal place. Since we were able to obtain a reproducibility of one in the fourth decimal place, we feel we attained an analytical accuracy of $\pm 1.0\%$, as far as the density determinations are concerned. Since, however, the analysis of a ternary mixture depends also on the chloride determination, we feel that the over-all accuracy is somewhat less than this, but it is much better than any chemical method.

In preparing the calibration curves, the chloride content was simply calculated from the formulae of the chlorides, for all possible mixtures. In de-

termining the chloride content of unknowns, we titrated conductimetrically with silver nitrate. In the analysis of the simple ternary system LiCl–KCl–H_2O, it was of course unnecessary to determine both chloride content and density, and we used chloride content alone for this purpose.

EXPERIMENTAL RESULTS

Table I contains our density determinations, which were used in the calibration; the chloride content is also included. When plotted against composition, either as binary or ternary mixture, the density curves are straight lines, as are those of chloride content.

TABLE I

DENSITIES AND CHLORIDE CONTENT OF MIXTURES OF LiCl, NaCl, AND KCl OF TOTAL WEIGHT 10 GM. IN 100 ML. OF SOLUTION, AT 25.0° C.

% LiCl	% NaCl	% KCl	$d_4^{25^\circ}$	% Cl
100	—	—	1.0519	83.62
80	20	—	1.0543	79.03
60	40	—	1.0568	74.43
50	50	—	1.0583	72.14
40	60	—	1.0594	69.85
20	80	—	1.0618	65.25
—	100	—	1.0644	60.66
—	80	20	1.0630	58.04
—	50	50	1.0612	54.11
—	20	80	1.0592	50.18
—	—	100	1.0579	47.56
20	—	80	1.0568	54.77
50	—	50	1.0550	65.59
80	—	20	1.0532	76.41
80	10	10	1.0537	77.73
50	20	30	1.0562	68.21
30	50	20	1.0594	64.93

Table II contains the results for the system LiCl–KCl–H_2O at 25° C. The equilibrium diagram is given as Fig. 2.

TABLE II

COMPOSITION OF SATURATED SOLUTIONS AND NATURE OF SOLID PHASES IN THE SYSTEM LiCl–KCl–H_2O AT 25° C.

Composition				Nature of solid phase
Liquid phase		'Wet' solid phase		
Wt. % LiCl	Wt. % KCl	Wt. % LiCl	Wt. % KCl	
45.4	0.0	—	—	$LiCl.H_2O$
44.2	2.3	59.05	0.9	$LiCl.H_2O$
44.7	3.4	56.5	6.3	$LiCl.H_2O$ + KCl
0.0	26.99	—	—	KCl
4.1	21.2	1.2	82.0	KCl
18.5	7.3	3.9	82.7	KCl
23.1	4.7	6.0	78.0	KCl
28.3	3.5	7.8	73.8	KCl
37.8	0.6	10.3	72.4	KCl
45.8	2.9	44.0	9.0	KCl + $LiCl.H_2O$

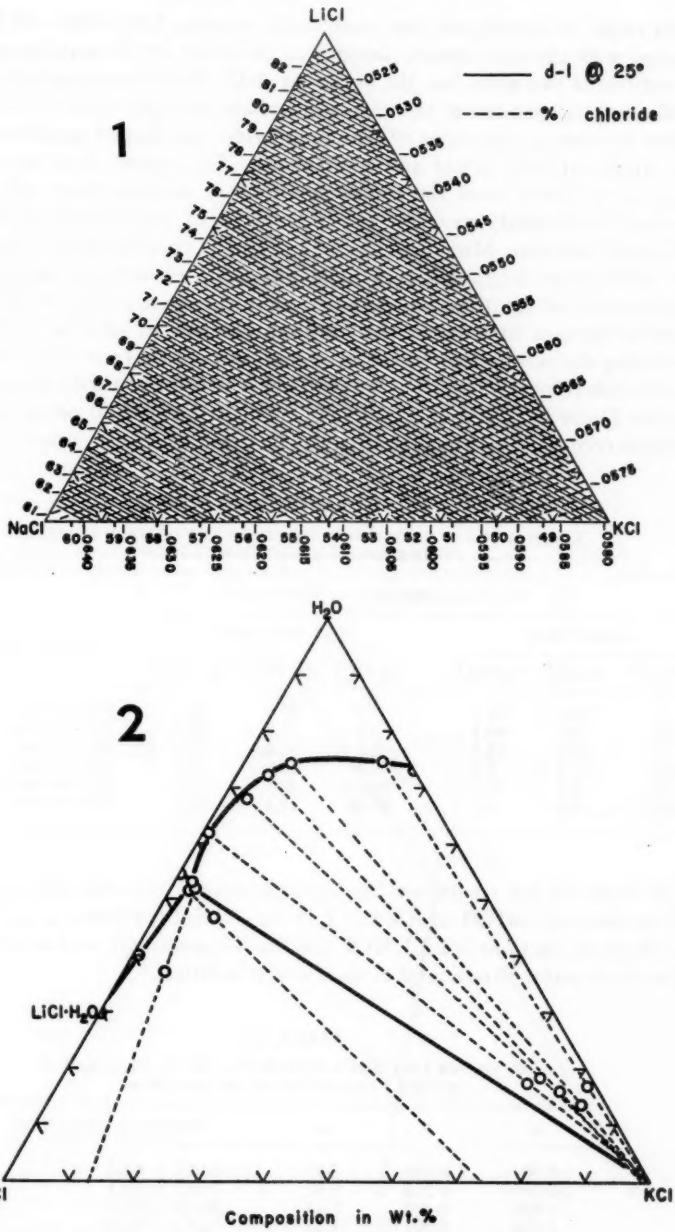


FIG. 1. Density and per cent chloride curves for the analytical method.
FIG. 2. The system LiCl–KCl–H_2O at 25°C.

In order to investigate the quaternary system, LiCl–NaCl–KCl–H_2O, we started with the only ternary isothermal invariant which contains appreciable quantities of two salts, viz. the invariant: KCl, NaCl, saturated solution, and, while keeping potassium chloride and sodium chloride present in excess, we added increasing quantities of lithium chloride, established equilibrium at 25°, and analyzed both liquid and solid phases. The system is of such a simple kind, as we knew from the component ternary systems, that only one quaternary (isothermal) invariant was to be expected, viz. LiCl.H_2O, KCl, NaCl, saturated solution. Moreover, since the ternary invariants with LiCl.H_2O as one solid phase contained very little potassium chloride or sodium chloride respectively in solution, we expected that the quaternary invariant would likewise contain little other than lithium chloride in solution. The point of analyzing the solid phase was that, so long as LiCl.H_2O was not a solid phase, the lithium chloride content of the solid phase would be entirely due to adhering mother liquor but, as soon as LiCl.H_2O appeared as a solid phase, the lithium chloride content would increase sharply. Our results are contained in Table III.

TABLE III

COMPOSITION OF EQUILIBRIUM SOLUTIONS AND OF SOLID PHASES IN THE SYSTEM LiCl–NaCl–KCl–H_2O

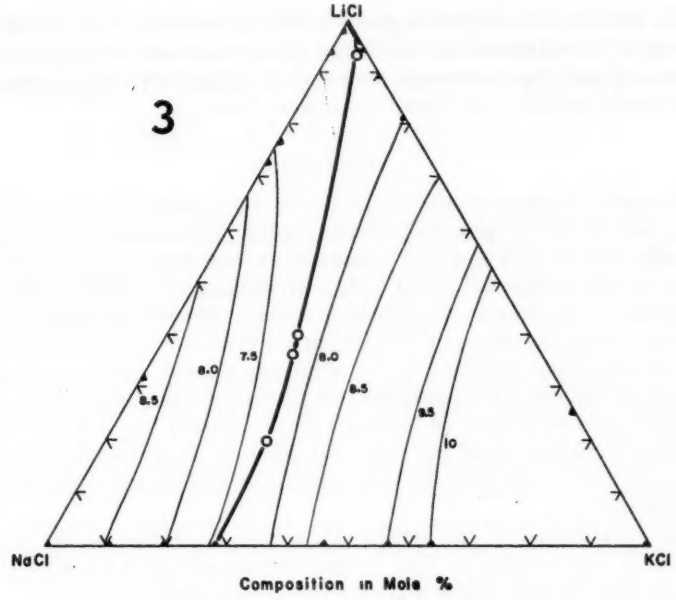
Composition						Nature of solid phase
Liquid phase			'Wet' solid phase			
% LiCl	% KCl	% NaCl	% LiCl	% KCl	% NaCl	
—	10.4	21.1	—	27.0	56.7	KCl + NaCl
8.2	7.6	10.7	0.8	17.9	62.5	KCl + NaCl
8.1	8.8	12.5	2.0	13.8	63.3	KCl + NaCl
32.9	1.3	2.2	7.3	29.5	43.2	KCl + NaCl
4.5	9.9	15.7	Trace	40.6	43.1	KCl + NaCl
41.5	3.1	0.2	34.05	12.2	20.8	KCl + NaCl + LiCl.H_2O

In Table IV the results are calculated in accordance with Jänecke's system of notation, viz.: $m$$H_2O$, aLiCl, bKCl, $(1-a-b)$NaCl, where a, b, and $(1-a-b)$ are the mole fractions of LiCl, KCl, and NaCl respectively, and m is the number of moles of water to one total mole of salt in solution.

TABLE IV

THE SYSTEM LiCl–NaCl–KCl–H_2O AT 25° C., CALCULATED BY THE JÄNECKE SYSTEM OF NOTATION

a	b	m	Nature of solid phase
0.00	0.388	7.60	NaCl + KCl
0.405	0.212	8.52	NaCl + KCl
0.649	0.402	7.49	NaCl + KCl
0.935	0.021	4.25	NaCl + KCl
0.210	0.263	7.61	NaCl + KCl
0.955	0.041	2.98	NaCl + LiCl.H_2O + KCl



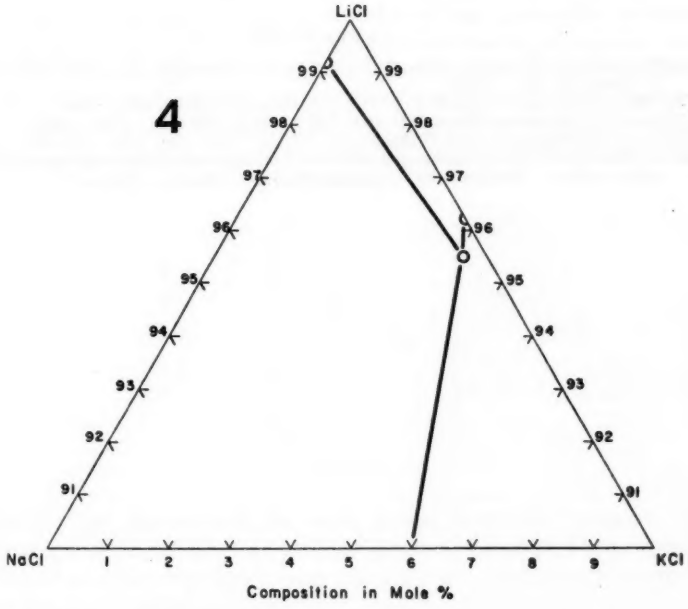


FIG. 3. The system LiCl–NaCl–KCl–H_2O at 25° in Jänecke representation.
FIG. 4. Enlargement of the quaternary invariant area.

The equilibrium diagram is given as Fig. 3, while Fig. 4 gives an enlarged picture of the lithium chloride corner of the diagram, showing two ternary invariants and the quaternary invariant. In Fig. 3, the isohydrores (lines of equal water content) are drawn in as faint lines.

DISCUSSION

No great discussion is called for, since neither double salts nor solid solutions form, but one or two points of interest emerge. First, the tremendous salting-out effect of the lithium ion is evident in the new system, LiCl–KCl–H_2O, as it was in the system LiCl–NaCl–H_2O, investigated by Smits, Elgersma, and Hardenberg. In the system containing sodium chloride, however, the sodium chloride content is reduced to 0.5 weight per cent at the invariant point, while the corresponding invariant in the potassium chloride system contains 3.2% potassium chloride. Otherwise, the two systems are very similar; for instance, in both there is a range of solutions which contain less sodium chloride or potassium chloride than the invariant solution. Attention has been drawn elsewhere (1) to the tenacity with which the lithium ion holds its water of hydration.

The composition of the isothermal invariant solution in the quaternary system is very similar to that in the ternary system LiCl–KCl–H_2O. The lithium chloride solid phase is always the monohydrate, LiCl.H_2O.

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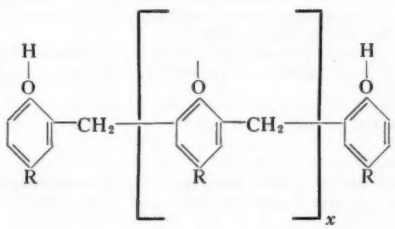
INFLUENCE OF THE NUMBER OF CARBON ATOMS OF THE ALKYL GROUP ON POLYMERIZATION AND PROPERTIES OF PARA-ALKYLPHENOL–FORMALDEHYDE POLYMERS[1]

By A. Rosenthal, F. Lederer, and K. Gilson

ABSTRACT

The polymerization (in organic media) of *p*-cresol–formaldehyde has been investigated in sealed tubes and in open systems. A series of almost colorless *p*-alkylphenol–formaldehyde polymers, prepared in sealed tubes, was studied to determine the influence of the number of carbon atoms of the substituting alkyl group on the polymerization process and on the properties of the polymers. Infrared spectra and chemical analyses of the original and heat-treated polymers were correlated with the structures of the polymers.

Para-alkylphenol–formaldehyde polymers have been little investigated. In 1930 the first completely oil-soluble phenolic resin was reported (3). Turkington and Allen (20) published the first comprehensive review of the properties and general preparation in open systems of oil-soluble phenolic resins, including a rather general evaluation of the varnishes made from these resins. Shreve and Golding (18) attempted to evaluate what they believed to be the best of the phenolic compounds for making varnishes. In work connected with a structural determination of Koresin, Marvel and co-workers (13) prepared and studied a few *p*-alkylphenol–formaldehyde resins. Although there is an extensive patent literature on oil-soluble resins, almost all of the preparative techniques involve the use of open systems and inorganic substances, in aqueous media, as catalysts. Considerable fundamental information on the condensation of formaldehyde with substituted phenols has been obtained from the model studies of Zinke (22, 24), Hultzsch (10), and others (6). Individual members of a polymer homologous series from *p-tert*-butylphenol and formaldehyde (I) were prepared by Zinke and co-workers (23).



I; $x = 0$ to 6

It was the first objective of the work herein reported to prepare, under carefully controlled conditions, a homologous series of *p*-alkylphenol–formaldehyde polymers having structure I (R = alkyl group), and to study in a quanti-

[1]*Manuscript received January 31, 1956.*
Contribution from the Department of Chemistry, The University of British Columbia, Vancouver, B.C.

tative way the effect of the aliphatic side chain on the polymerization process. A second objective was to study the structures and properties of these polymers.

The *p*-alkylphenol–formaldehyde polymers were prepared at 130° in sealed Carius tubes using bis-(2-ethoxyethyl) ether as solvent, *s*-trioxane as a source of formaldehyde, and *p*-toluenesulphonic acid monohydrate as catalyst. The crude resins were freed of insoluble material and reprecipitated from water. Almost completely colorless solid resins, which were soluble in N,N-dimethylformamide or pyridine, were obtained. The use of a closed system rather than an open one permitted an excellent control of conditions as evidenced by the fact that agreement in specific viscosities of the resins obtained in repeat runs was ±3%. Polymerization of *p*-cresol with formaldehyde under a closed system led to the production of a resin having approximately twice the specific viscosity of one obtained under similar experimental conditions except for that of carrying out the polymerization under reflux in an open system (Table I, polymers 4 and 14).

TABLE I

PREPARATION OF *p*-CRESOL–FORMALDEHYDE POLYMERS

Polymer No.	Moles[a] CH_2O	Solvent[b] in ml.	Tube length, cm.	Time, hr.	Temp., °C.	% soluble[c]	Specific viscosity[d]
1	1.01	5	40	20	110	100	0.037
2	1.03	5	40	20	110	100	0.040
3	1.01	5	40	20	120	98	0.078
4[e]	1.01	5	40	17	130	80	0.091
5	1.03	5	40	17	130	90	0.103
6	1.00	5	40	20	150	70	0.098
7	1.01	5	40	4	130	100	0.041
8	1.01	5	40	10	130	85	0.071
9	1.01	5	40	20	130	77	0.092
10[f]	1.01	10	40	20	130	72	0.106
11[g]	1.01	15	40	20	130	76	0.110
12[h]	1.01	5	10	20	130	57	0.108
13[i]	1.01	5	20	20	130	80	0.085
14[j]	1.01	5	—	20	130	93	0.049

[a]*Per mole of p-cresol; 0.100 mole of p-cresol was used in each run.*
[b]*Bis-(2-ethoxyethyl) ether was used as solvent.*
[c]*At 80–90° with 4 gm. of crude polymer per 100 ml. of N,N-dimethylformamide.*
[d]*At 25° with 0.5 gm. of soluble portion of polymer per 100 ml. of N,N-dimethylformamide.*
[e]η_{sp} *of duplicate was 0.090.*
[f]η_{sp} *of duplicate was 0.108.*
[g]η_{sp} *of duplicate was 0.109.*
[h]η_{sp} *of duplicate was 0.110.*
[i]η_{sp} *of duplicate was 0.087.*
[j]*Polymerization carried out in a flask fitted with a reflux condenser.*
The softening point of polymer 1 was 230–235°, and those of 3, 4, and 8 were 240–245°.

The effects of varying temperature, reaction time, volume of solvent, and tube length on the polymerization of *p*-cresol–formaldehyde polymers (as revealed by specific viscosities) are shown in Table I. An increase of 1 to 3% molar excess of formaldehyde over *p*-cresol resulted in no significant increase in specific viscosities of the polymers when the condensation was carried out at 110° (polymers 1 and 2). When the polymerization was carried out at 130°, a 2% molar increase in formaldehyde gave approximately a 10% increase in specific viscosity (polymers 4 and 5). Although use of equimolar quantities of

reactants at a temperature of 150° might be expected to yield a much higher molecular weight polymer than was obtained at 130°, such a result was not attained as seen in polymer 6.

At constant molar ratios of reactants an increase in polymerization temperature from 110° to 130° led to an increase in specific viscosities of the polymers from 0.037 to 0.091 and also a 20% increase in the amounts of insoluble material (Table I, polymers 1 and 4). Previous workers (1, 8, 23) have suggested reasons for the partial insolubility of some *p*-alkylphenol–formaldehyde polymers. Infrared studies did not reveal any significant difference in the structures (as shown by the spectra) of the soluble and insoluble fractions of the *p*-cresol–formaldehyde polymers (Fig. 1, polymer 1 and Fig. 2, 4*d*).

It was surprising to discover that a less soluble phenol–formaldehyde polymer was obtained when the Carius tube length was decreased from 40 to 10 cm. (other conditions being the same), although the specific viscosities of the soluble portions of the polymers were essentially the same (Table I, polymers 11 and 12).

The effect of the *p*-alkyl group on the degree of polymerization of *p*-alkylphenol–formaldehyde polymers is shown in Table II. It is interesting to note

TABLE II

PREPARATION OF *p*-ALKYLPHENOL–FORMALDEHYDE POLYMERS[a] IN SEALED CARIUS TUBES

p-Alkyl groups	Polymer No.	% soluble[b]	Specific viscosity[c]	Softening point, °C.[d]	Theoretical formula	Analytical† Calc. C	Calc. H	Found C	Found H
Methyl	4	80	0.091	240–245	$(C_8H_8O)_x$	80.00	6.71	76.42	7.20
Ethyl*	15	80	0.069	210–215	$(C_9H_{10}O)_x$	80.58	7.51	76.81	7.70
n-Propyl	16	98	0.064	210–215	$(C_{10}H_{12}O)_x$	81.02	8.16	80.01	8.80
Isopropyl	17	98	0.069	245–250		81.02	8.16	78.59	8.28
n-Butyl*	18	96	0.048	205–210	$(C_{11}H_{14}O)_x$	81.41	8.70	80.24	8.67
Isobutyl	19	100	0.067	230–235				80.17	8.49
sec-Butyl	20	90	0.139	205–210				80.07	8.71
tert-Butyl	21	98	0.046	195–200				79.97	8.84
n-Amyl	22	95	0.045	195–200	$(C_{12}H_{16}O)_x$	81.77	9.15	80.52	9.11
Isoamyl	23	100	0.051	225–230				80.52	9.29
sec-Amyl*	24	95	0.112	105–110				80.39	8.98
tert-Amyl	25	100	0.051	165–170				79.89	9.00
n-Hexyl	26	100	0.042	190–195	$(C_{13}H_{18}O)_x$	82.08	9.54	80.84	9.65
tert-Octyl	27	100	0.014	80–85	$(C_{15}H_{22}O)_x$	82.52	10.16	82.26	10.20

[a] *Prepared from 0.100 mole p-alkylphenol, 0.101 mole formaldehyde (s-trioxane), 5 ml. bis-(2-ethoxyethyl) ether, and 0.20 gm. p-toluenesulphonic acid monohydrate. Reaction run at 130° for 20 hr. Tube length was 40 cm.*

[b] *At 80–90° with 4 gm. of crude polymer per 100 ml. of N,N-dimethylformamide.*

[c] *At 25° with 0.5 gm. of purified polymer per 100 ml. of N,N-dimethylformamide.*

[d] *Taken in capillary tubes.*

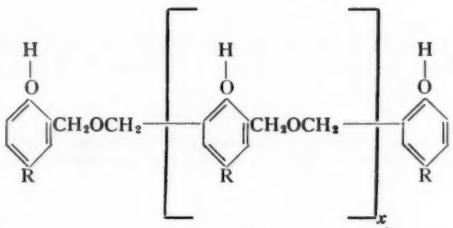
* η_{sp} *of duplicates of 15, 18, and 24 were 0.067, 0.047, and 0.114, respectively. 4-sec-Amylphenol—*$CH_3(CH_2)_2CH(CH_3)C_6H_4OH$.

† *Microanalyses by: Dr. W. Mänser, Nerdstr. 140, Zurich 37, Schweiz.; Drs. G. Weiler and F. B. Strauss, 164, Banbury Road, Oxford, England.*

that as the straight chain alkyl group increased in size from methyl to *n*-hexyl the specific viscosities of the polymers decreased from 0.091 to 0.042 (polymers 4, 16, 18, 22, and 26). Polymers obtained from *p*-*sec*-butylphenol and *p*-*sec*-

amylphenol had more than double the specific viscosities of those obtained from the isomeric branched-chain or straight-chain *p*-alkylphenols (polymers 19 to 25). Other workers (18, 14), who have studied the properties of the varnishes from resins of several *p*-alkylphenols, have found that the alkyl group has an effect on the time of resinification.

A surprising and interesting finding was the wider divergence of the experimental per cent carbon from the theoretical of polymers prepared from *p*-cresol than of those prepared from the other *p*-alkylphenols (Table II, Analytical). It might have been expected that the reverse would have been the case, since the *p*-cresol–formaldehyde polymer had a higher specific viscosity than most of the other *p*-alkylphenol polymers. A *p*-cresol–formaldehyde condensate having three benzene nuclei has a carbon content of 79.2% and as a result, the low per cent carbon found can not be fully explained on the basis of a high concentration of low molecular weight fractions. Zinke (22) has proposed that benzyl ether linkages (as shown in II) and methylene bridges are formed at



II

temperatures up to 170°, and above these temperatures formaldehyde is evolved leaving a polymer having structure I. If the structure of the *p*-cresol–formaldehyde polymer is more accurately represented by II than by I, the theoretical per cent carbon would be 72% instead of 80%. The fact that the carbon found was 76.4% indicates that more than half of the linkages which bound the phenolic nuclei were methylene bridges. In an attempt to study this problem further, purified *p*-cresol– and *p*-*sec*-amylphenol–formaldehyde

TABLE III

EFFECT OF HEAT[a] ON VISCOSITY AND COMPOSITION OF *p*-ALKYLPHENOL–FORMALDEHYDE POLYMERS

p-Alkyl group	Polymer No.	Initial specific viscosity[b]	Specific viscosity[b] after heating	Analytical			
				Before heat treatment		After heat treatment	
				C	H	C	H
Methyl	4	0.091	0.019[c]	76.38	6.71	78.74	6.55
sec-Amyl	24	0.112	0.078[c]	80.39	8.98	80.89	9.06

[a]*Purified and dried polymer heated at 182° for three hours under an atmosphere of dry nitrogen.*
[b]*At 25° with 0.5 gm. of polymer per 100 ml. of N,N-dimethylformamide.*
[c]*Polymers darkened in color on heating.*

polymers having high specific viscosities were heated at 182° for three hours under an atmosphere of dry nitrogen. The *p*-cresol–formaldehyde polymer evolved formaldehyde. When the latter polymer was heated at about 250° for about one minute, a rapid evolution of bubbles accompanied the change in state of the polymer from solid to liquid. Analytical studies (Table III) of the *p*-cresol–formaldehyde polymer heated at 182° showed that the carbon content of the polymer had increased by 2.4% and the hydrogen content remained about the same. There was a decrease in the specific viscosities of the polymers from 0.091 to 0.019. The *p-sec*-amylphenol polymer when heated under the same conditions had approximately the same carbon content and a 30% decrease in specific viscosity (Table III). Infrared studies showed that the band at 1095 cm.$^{-1}$, present in the spectra of both original polymers, was not present in those of the corresponding heat-treated polymers (Fig. 1, polymers 4 to 4*c*

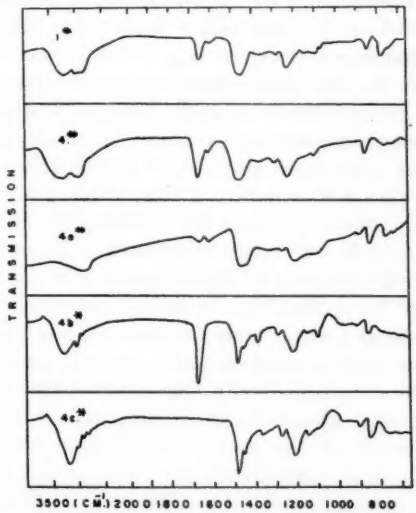


FIG. 1. Infrared spectra of *p*-cresol–formaldehyde polymers:
1** *p*-Cresol–formaldehyde (η_{sp} = 0.037).
4** *p*-Cresol–formaldehyde (η_{sp} = 0.091).
4*a*** *p*-Cresol–formaldehyde (heat-treated; η_{sp} = 0.019).
4*b** *p*-Cresol–formaldehyde (η_{sp} = 0.091).
4*c** *p*-Cresol–formaldehyde (heat-treated; η_{sp} = 0.019).

***Nujol mull; other spectra: 5% solution in chloroform.*
**Partially soluble. Insoluble part filtered off.*

and Figs. 4 and 5, polymers 24 to 24*c*). Evidence that the band at 1095 cm.$^{-1}$ is characteristic of a benzyl ether linkage is provided by the fact that the spectrum of dibenzyl ether has a band at 1095 cm.$^{-1}$ whereas that of 4,4′-dihydroxydiphenylmethane does not (16). Zinke (23) and Hultzsch (10) have suggested that the fission of the ether bridge results in the production of phenol aldehydes together with *o*-quinone methides. The presence of the latter degradation products would account for the fact that the polymers darkened after

prolonged heating at 182°. Present studies do not permit a correlation of polymer structure with the band at 1670 cm.$^{-1}$ which was present in the spectrum of the original polymer but absent in that of the heat-treated *p*-cresol–formaldehyde polymer.

The softening points of the *p*-cresol–formaldehyde polymers were essentially the same for polymers having specific viscosities ranging from 0.057 to 0.091. A slightly lower value (230–235°) was obtained with a *p*-cresol polymer having a specific viscosity of 0.037 (Table I). The fact that the melting points were found to be essentially independent of the molecular weights of these polymers lends support to the assumption that the polymers being dealt with were of high molecular weight (4). Attempts to obtain molecular weights of the polymers by the Rast method or by the use of benzil as solvent were unsuccessful.

The effect of the alkyl groups upon the softening points of linear phenoplasts is strikingly brought out by the fact that the softening point of *p-sec*-amylphenol–formaldehyde polymer ($\eta_{sp} = 0.112$) was 105–110°, whereas that of the *p*-cresol–formaldehyde polymer ($\eta_{sp} = 0.091$) was 240–245° (Table II, polymers 4 and 24). In this connection it is interesting to note that other workers (4, 9) have recently found that the size and flexibility of alkyl groups have a marked effect on the melting points of linear polyesters. For polymers of approximately the same molecular weight (Table II, polymers 21 and 25), an increase in the size and bulkiness of the alkyl group from *tert*-butyl to *tert*-amyl resulted in approximately a 30° lowering in the softening points of the polymers. Surprisingly, the *p-sec*-amylphenol polymer (polymer 24) which had the highest specific viscosity of all the isomeric amylphenol polymers had a softening point 60° lower than that of the *tert*-amylphenol polymer. From a consideration of molecular dimensions and bond angles, Megson (15) deduced that a Novolak resin must consist of highly kinked, asymmetrical molecules. He pointed out that a hardened resin has a sponge-like structure which can explain, partially, certain physical and chemical properties of the resin.

The infrared spectra of the *p*-alkylphenol–formaldehyde polymers are presented in Figs. 1 to 5. Compounds containing alkyl hydrocarbon groups usually exhibit absorption from 3130 to 2800 cm.$^{-1}$, which is the region attributed to the (C–H) stretching vibrations. Richards and Thompson (16) and Bender (2) have ascribed a weak absorption band at about 12.2 μ (820 cm.$^{-1}$) to 2,4-substitution of the phenolic ring. They suggest that a band at about 11.50 μ (870 cm.$^{-1}$) is characteristic of a 2,4,6-substituted phenol residue. On the basis of their work, one can conclude that most of the polymers studied having an alkyl side chain equal to or greater than four carbons had 2,4-substitution. All polymers which had a specific viscosity greater than 0.069 showed no band at 820 cm.$^{-1}$. It is interesting to note, however, that the *p*-cresol–formaldehyde polymer 1, which had a specific viscosity of 0.037, exhibited no band at 820 cm.$^{-1}$, whereas the *p*-isopropylphenol–formaldehyde polymer (No. 17), which had a specific viscosity of 0.069, absorbed in this region. This would indicate that one can not always correlate molecular size with 2,4-substitution, although it might be expected that polymers belonging to the series I which have the lowest molecular weight should have the highest concentration

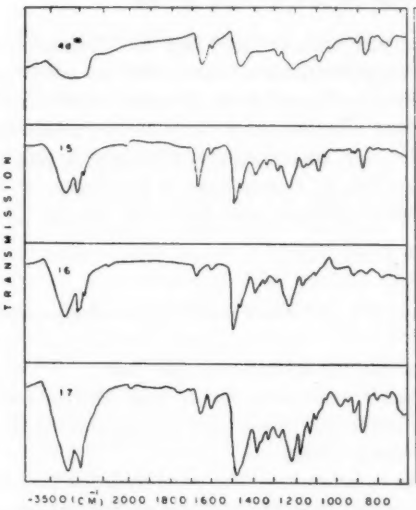


FIG. 2. Infrared spectra of *p*-alkylphenol–formaldehyde polymers:
4*d* *p*-Cresol–formaldehyde (insoluble fraction).
15 *p*-Ethylphenol–formaldehyde.
16 *p*-*n*-Propylphenol–formaldehyde.
17 *p*-Isopropylphenol–formaldehyde.

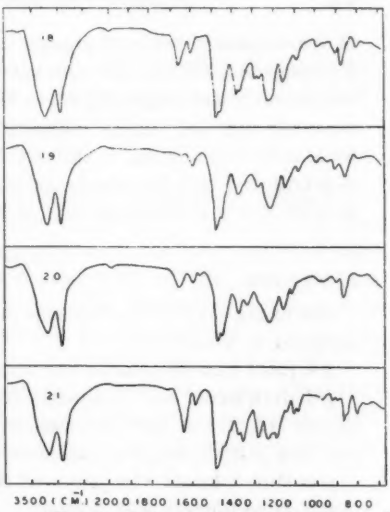


FIG. 3. Infrared spectra of *p*-alkylphenol–formaldehyde polymers:
18 *p*-*n*-Butylphenol–formaldehyde.
19 *p*-Isobutylphenol–formaldehyde.
20 *p*-*sec*-Butylphenol–formaldehyde.
21 *p*-*tert*-Butylphenol–formaldehyde.

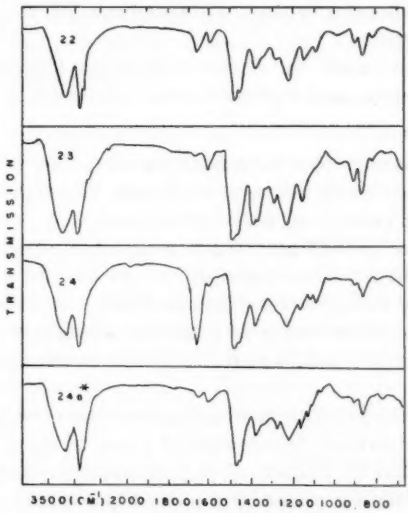


FIG. 4. Infrared spectra of *p*-alkylphenol–formaldehyde polymers:
22 *p*-*n*-Amylphenol–formaldehyde.
23 *p*-Isoamylphenol–formaldehyde.
24 *p*-*sec*-Amylphenol–formaldehyde.
24*a** *p*-*sec*-Amylphenol–formaldehyde (heat-treated).

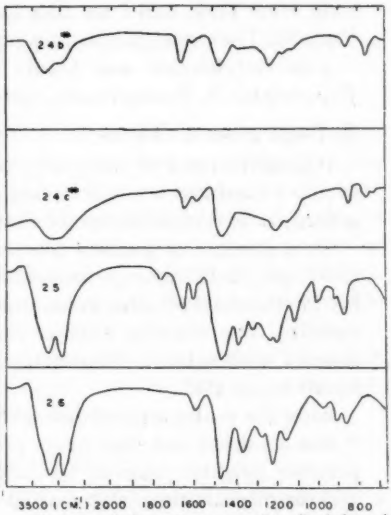


FIG. 5. Infrared spectra of *p*-alkylphenol–formaldehyde polymers:
24*b*** *p*-*sec*-Amylphenol–formaldehyde.
24*c*** *p*-*sec*-Amylphenol–formaldehyde (heat-treated).
25 *p*-*tert*-Amylphenol–formaldehyde.
26 *p*-*n*-Hexylphenol–formaldehyde.

of 2,4-disubstituted end groups. It has been pointed out by Thompson and Torkington (19) that the characteristic frequencies shown by the substituted benzenes in the range of 715 to 880 cm.$^{-1}$ vary with the position of the substituents and are largely independent of their exact nature. The pronounced band at 860 to 875 cm.$^{-1}$ exhibited by all *p*-alkylphenol–formaldehyde polymers is attributed to 2,4,6-trisubstitution (16, 2). Absorption in the region of 3100 to 3300 cm.$^{-1}$ is characteristic of associated phenolic hydroxyl groups (16).

EXPERIMENTAL

1. Reagents

Bis-(2-ethoxyethyl) ether was purified and dried according to the procedure outlined in Vogel (21).

p-Cresol was distilled in vacuum and the middle fraction used.

p-Ethylphenol and *p*-*n*-propylphenol were prepared by the Martin modification (12, 21) of the Clemmensen reduction of purified *p*-hydroxyacetophenone and *p*-hydroxypropiophenone, respectively.

p-*n*-Butylphenol was prepared by sulphonating the pure hydrocarbon (21).

p-*n*-Hexylphenol was prepared according to the method of Sandulesco and Girard (17). The ester was first formed and then rearranged.

p-Isoamylphenol was prepared according to a modification of the procedure of Klages (11, 5).

The remaining chemicals used were obtained from Eastman Organic Chemicals, New York, and from Bios Laboratories, Inc., 17 West 60th Street, New York 23. They were checked for purity.

p-*tert*-Octylphenol was kindly donated by Rohm and Haas Company, Philadelphia 5, Pennsylvania, and was used without further purification.

2. Preparation of Polymers

Polymerizations of the p-alkylphenols and formaldehyde were carried out in pyrex combustion tubes having an inside diameter of 19 mm. The following procedure is representative of that used in all polymerizations.

To a mixture of purified *p*-cresol (10.813 gm., 0.100 mole) and *s*-trioxane (3.026 gm., 0.101 mole as formaldehyde) there was added a solution of 5 ml. of bis-(2-ethoxyethyl) ether containing 0.20 gm. of *p*-toluenesulphonic acid monohydrate. The reaction mixture (in the presence of nitrogen) contained in a sealed Carius tube was thoroughly mixed and heated in a Carius bomb furnace for 20 hr. at 130°.

After the *p*-alkylphenol–formaldehyde polymer was removed from the tube, it was air-dried and then finely pulverized. An amount of 4 gm. of the crude polymer (slightly colored) was added to 100 ml. of N,N-dimethylformamide and the mixture then heated at 80–90° for about 10 min. Undissolved polymer was removed by filtration with a coarse sintered glass funnel or filter paper. The clear filtrate was added dropwise with rapid stirring to 2 liters of water containing 5 ml. of concentrated hydrochloric acid (to cause settling of the polymer). The almost completely colorless polymer, removed by filtration, was then washed with water until free of chloride and dried at 60° under vacuum over phosphorus pentoxide.

3. Viscosity Determinations of Polymers

All viscosities were carried out using a Fenske (A.S.T.M. No. 50) viscometer. The specific viscosity of 0.500 gm. of each dried polymer in 100 ml. of N,N-dimethylformamide at 25° (±0.05°) was taken.

4. Softening Points of Polymers

The softening points of the polymers were taken in capillary tubes which were heated in a copper melting point block fitted with a light and lens for illumination and observation (7). The approximate softening point of each polymer was determined by raising the temperature of the melting point block by 5° intervals and noting the temperature interval in which a new sample softened in one minute. The softening points recorded are those at which all of each polymer fully underwent a change in physical state. Part of the polymer usually softened at a temperature considerably lower than that reported. When the polymers were heated gradually, no softening points could be obtained. No claim to quantitative accuracy of the softening points of the polymers is made.

5. Infrared Spectrophotometric Analyses

A Perkin-Elmer Model 21 double-beam recording spectrophotometer with a sodium chloride prism was used to obtain the spectra presented in Figs. 1 to 5. Most of the samples were run as 5% solutions in chloroform. Any polymer samples which were partially soluble in chloroform were also run as Nujol mulls and are so noted on the spectra concerned.

The authors are indebted to the British Columbia Research Council for the infrared analyses.

SUMMARY

Polymerization of *p*-cresol with formaldehyde in sealed tubes resulted in polymers having almost double the molecular weight of those obtained in open systems. In closed systems higher molecular weight polymers were obtained from *p-sec*-butylphenol and *p-sec*-amyphenol than from *p*-cresol. A polymer obtained from *p-sec*-amyphenol and formaldehyde (η_{sp} 0.112) was found to be much more stable to heat than one from *p*-cresol–formaldehyde (η_{sp} 0.091). Infrared studies of the polymers showed that two of the absorption bands present in the original *p*-cresol–formaldehyde polymer (at 1095 and 1670 cm.$^{-1}$) were not present in the spectrum of the same polymer subsequently heated at 182° for three hours. The spectra of the original and heat-treated *p-sec*-amylphenol–formaldehyde polymers were essentially the same.

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NOTE

SUR LE SPECTRE ULTRAVIOLET DE L'ACIDE PERACÉTIQUE ET L'HYDROLYSE DES PERACÉTATES

PAR PAUL A. GIGUÈRE ET A. W. OLMOS[1]

Il ne semble pas exister dans la littérature de données précises sur l'absorption ultraviolette de l'acide peracétique. Egerton et ses collaborateurs (2) rapportent avoir mesuré l'absorption d'une solution à 75% et l'avoir trouvée à peu près égale à celle de l'acide acétique, ce qui paraît surprenant a priori étant donné la grande opacité du groupement peroxydique dans l'ultraviolet. Comme nous avions déjà préparé ce composé à un assez haut degré de pureté afin d'étudier sa structure moléculaire au moyen de l'infrarouge (4) nous avons jugé bon de mesurer en même temps son spectre ultraviolet.

La préparation de l'acide peracétique à 97% a déjà été décrite en détail. La soude qui servit à neutraliser les solutions fut préparée à partir de sodium métallique et d'alcool éthylique absolu; le produit de l'hydrolyse était ensuite dosé par l'acide phtalique solide. En général les solutions semblaient parfaitement stables, même sous l'action de l'ultraviolet dans le spectrophotomètre (Modèle DU de Beckman). L'apparition occasionnelle de bulles d'oxygène sur les parois de la cuvette d'absorption entrainait inévitablement le rejet de l'échantillon. Toutes les mesures furent faites avec des solutions fraîchement préparées et chaque spectre fut enregistré deux fois afin de s'assurer qu'il ne se produisait aucune décomposition appréciable.

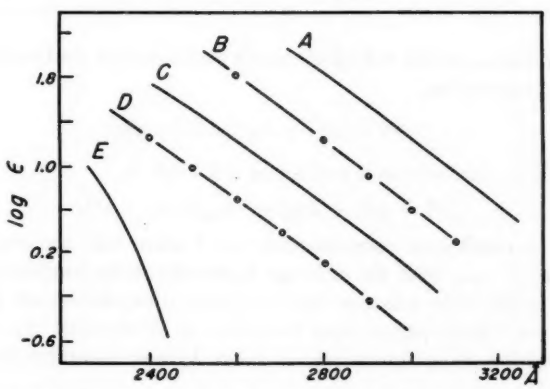

FIG. 1. Absorption ultraviolette de solutions d'acide peracétique et de peracétates. A. Ion perhydroxyle. B. Ion peracétate. C. Peroxyde d'hydrogène. D. Acide peracétique. E. Acide acétique.

[1]*Boursier Cominco. Adresse actuelle: St. Francis Xavier University, Antigonish, N.S.*

Les courbes de la figure 1 donnent les coefficients d'extinction d'après la loi de Beer, $\log I/I_0 = -\epsilon\, c\, d$, où les concentrations, c, sont en moles par litre et l'épaisseur de l'échantillon, d, est en cm. Comme pour le peroxyde d'hydrogène, dont le spectre bien connu (6) est reproduit ici pour fin de comparaison, l'absorption ultraviolette de l'acide peracétique ne présente qu'un seuil continu sans aucune indication de maximum. Il en est de même des ions correspondants, O_2H^- et CH_3COOO^-, dont l'absorption est toutefois beaucoup plus forte que celle des molécules non dissociées. On sait par ailleurs que les solutions de soude sont transparentes jusqu'à 2300 Å environ.

L'acide peracétique dissous dans un solvant indifférent (iso-octane) absorbe presque de la même façon qu'en solution aqueuse, ce qui confirme bien que les peracides sont des acides assez faibles. En effet, Everett et Minkoff (3) ont trouvé récemment par titration potentiométrique une valeur de 8.2 pour le pK de l'acide peracétique. Ce résultat est en tout point conforme aux nôtres, comme le montrent les données du tableau I, où les pH de solutions partiellement neutralisées ont été calculés à partir de l'équation de Henderson, d'abord d'après la composition,

TABLEAU I

pH DES SOLUTIONS DE PERACÉTATES ALCALINS

Base / Acide	pH, d'après la composition	ϵ	pH, d'après l'absorption
0	4.7	2.58	—
0.05	6.9	3.75	6.9
0.1	7.2	4.97	7.1$_5$
0.2	7.6	6.97	7.4
0.3	7.8	10.8	7.7$_5$
0.5	8.2	17.0	8.2$_5$
0.7	8.5$_5$	23.1	8.5
1.0	10.4	33.6	—

$$\mathrm{pH} = \mathrm{p}K + \log([\mathrm{sel}]/[\mathrm{acide}]) \qquad [1]$$

puis d'après les coefficients d'extinction ϵ à 2700 Å,

$$\mathrm{pH} = \mathrm{p}K + \log[(\epsilon - \epsilon_{HA})/(\epsilon_{A^-} - \epsilon)], \qquad [2]$$

ϵ_{HA} étant le coefficient correspondant de l'acide pur (en solution environ 0.08 molale) et ϵ_{A^-}, celui du mélange équimoléculaire soude-acide.

A la suite de leurs travaux sur la vitesse d'oxydation de l'acide *O*-iodobenzoique par l'acide peracétique Boëseken et Wicherlink (1) ont conclu que la décomposition de ce dernier par un excès de base caustique procède en deux étapes:

$$CH_3COOOH + NaOH \rightarrow CH_3COONa + H_2O_2 \qquad [3]$$

et

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2. \qquad [4]$$

Dans les conditions de leurs expériences, soit par addition de 5 à 10 cc. de soude (variant de 20 à 50%) à 1 cc. d'acide peracétique à 10%, l'hydrolyse

[3] semblait complète en quelques minutes tandis que la décomposition du peroxyde d'hydrogène était alléatoire. Leur conclusion était basée sur le fait que ces solutions ne libéraient pas d'iode lors de l'addition d'une solution acide de KI, réaction connue sous le nom de Riesenfeld-Liebhafsky (6). Il est maintenant évident qu'une telle conclusion est erronée. En effet, si l'hydrolyse était aussi rapide que prétendu, les courbes d'absorption de solutions de peracide partiellement neutralisées ne devraient pas dépasser celles du peroxyde d'hydrogène (courbe C, Fig. 1). Bien plus, nous avons trouvé que l'addition d'un grand excès de soude (6:1) à l'acide peracétique n'augmente pas le coefficient d'absorption au delà de la courbe C alors que dans l'hypothèse de l'hydrolyse [3] l'absorption devrait tendre vers celle de l'ion O_2H^- (courbe A). Récemment, Partington et Fathallah (5) ont prouvé qu'un test de Riesenfeld-Liebhafsky *négatif* n'est pas valide dans le cas des perborates et des percarbonates; nos résultats confirment bien qu'il en est de même pour les peracétates.

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